Solar-Driven Overall Water Splitting on CoO Nanoparticles:
First-principles Density functional theory studies

By
Kyoung-Won Park

B.S. Materials Science and Engineering, Korea University, 2007
M.S. Materials Science and Engineering, Korea University, 2009

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Authored by .................................................................
Kyoung-Won Park
Department of Materials Science and Engineering
May 03, 2018

Certified by .................................................................
Alexie M. Kolpak
Assistant Professor, Department of Mechanical Engineering
Thesis Supervisor

Certified by .................................................................
Harry L. Tuller
Professor, Department of Materials Science and Engineering
Thesis Reader

Accepted by .................................................................
Donald R. Sadoway
Chair, Departmental Committee on Graduate Students
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ABSTRACT

Photoelectrochemical (PEC) water splitting has been suggested as a promising technique for large-scale hydrogen fuel production. In particular, spontaneous photocatalytic overall water splitting on self-standing particles in water without external driving potential has been highlighted as a clean and economical energy generation method for the future. Among various photocatalytic materials, some cobalt-based materials including CoP, Co3P, Co(OH)2, CoO, have attained major interest because they exhibit improved catalytic activity for hydrogen evolution in the form of nanoparticles, unlike most cobalt-based materials which have been assessed as water oxidizing catalysts in the past decade.

CoO nanoparticles have been observed to photocatalytically split water into H2 and O2 at room temperature without an externally applied potential or co-catalyst, with high photo-catalytic efficiency (solar-to-hydrogen efficiency of ~5%) which hits the record among single-material self-standing photocatalysts. The photocatalytic activity of CoO nanoparticles was experimentally shown to stem from the optimal conduction and valence band edge positions (Ec and Ev) relative to water reduction and oxidation potential levels (H+/H2 and H2O/O2), such that the Ec and Ev span the water redox potentials. The overall water splitting is not expected from CoO micropowder or bulk CoO because they have band edges far below the H+/H2 level, which are not optimal for overall water splitting. However, the origin of the shift in the band edges due to decrease in particle size (from bulk or micropowder to nanoparticles) was unknown. Moreover, the mechanism by which H2 and O2 simultaneously and spontaneously evolve on the nanoparticles, as well as how the CoO nanoparticles could exhibit a high photocatalytic efficiency even without a co-catalyst or an external driving potential have remained unanswered.

In this work, we use first-principles density functional theory (DFT) calculations to explore thermodynamically stable surface configurations of CoO in an aqueous environment in which photocatalytic water splitting occurs. We also calculate the Ec and Ev of CoO surfaces relative to water redox potentials, showing that the band edge positions are sensitive to surface chemistry which is determined by surface orientation, adsorbates, and stoichiometry, and thus growth conditions and operating environment. In particular, we predict that CoO nanoparticles have fully hydroxylated CoO(111) facets (OH*-CoO(111)), with band edges spanning the water redox potentials, while larger CoO particles (such as CoO micropowders) have a full monolayer of hydrogen on the CoO(111) facets, with a band alignment that favors water oxidation but not water reduction. From these calculations, we demonstrate that explicit inclusion of liquid water is crucial for accurately predicting the band edge positions, and thus photocatalytic behavior of CoO in an aqueous solution. In order to find the origin of the high efficiency and spontaneous overall water splitting without an external bias or a co-catalyst, we also elucidate the mechanisms for charge separation and H2 and O2 evolution on CoO nanoparticles under illumination in an aqueous solution. We demonstrate that electrons are driven to CoO(100) facets and holes are driven to OH*-CoO(111) facets as a result of a built-in potential arising from the very different potential levels of the two facets. We show that H2 evolution preferentially occurs on the CoO(100) facets, while O2 evolves on the OH*-CoO(111) surfaces, based on our new criteria. Importantly, we suggest that the conventional criterion for determining the feasibility of H2 or O2 generation from water splitting – i.e., $E_c < H^+/H_2$ level or $E_v > H_2O/O_2$ level – is insufficient. Instead, we suggest that a more appropriate set of criteria is whether the photo-excited electrons and holes have sufficient energy to overcome the kinetic barrier for the H2 and O2 evolution reaction, respectively, on the relevant surface facet.

This work explains why and how photocatalytic overall water splitting has been observed only on CoO nanoparticles. Our understanding of the overall water splitting mechanism on CoO nanoparticles provides a general explanation of experimentally observed overall water splitting phenomena on a variety of self-standing photocatalysts as well as a new approach for screening novel photocatalytic materials for efficient water splitting and other reactions.

Thesis Supervisor: Alexie M. Kolpak
Title: Assistant Professor, Department of Mechanical Engineering
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CHAPTER 1. INTRODUCTION

1.1 Motivation

In recent decades, nano-sized structures have been highlighted in designing photocatalysts for water splitting. This is because the enhanced photocatalytic activity is often observed in the nano-sized photocatalysts, relative to the bulk phases from which they are derived [1-5]. In a number of cases, even photocatalytically inactive bulk materials have also been observed to have photocatalytic activity in the photocatalysts with size reduction [1,6-9]. Among photocatalysts that exhibit an enhanced activity as a result of the reduction of particle size, CoO is of great interest, with a very high solar-to-hydrogen efficiency of ~5% (this number hit the record for the highest efficiency among self-standing monolithic photocatalysts), as well as the ability to dissociate water into stoichiometric H₂ and O₂ (two H₂ for each O₂) without external bias or co-catalysts under visible light irradiation [1]. The transition from inactive to active CoO is due to a significant upward shift in the band edge positions relative to the water redox potential in going from micropowders [1,10-11] to nanoparticles (from positive to negative potential by ~1.4 V vs. NHE) as shown in Figure 1-1. However, a fundamental explanation for the shift in the CoO band edges with the particle size reduction, as well as the mechanism by which overall water splitting occurs on the single-material CoO nanoparticles without the help of external driving potential or a co-catalyst remained unknown. In addition, the origin of the prominent photocatalytic efficiency of the CoO nanoparticles has not been understood, because a single-material nanoparticle (such as CoO nanoparticles in the experiment) is generally believed to show very low efficiency of ~ 0.1 % [12-13].
Figure 1-1 Conduction and valence band edge positions (CB and VB) of CoO micropowder (left and red) and CoO nanoparticles (right and black) relative to water redox potential levels (H\(^+\)/H\(_2\) and H\(_2\)O/O\(_2\)). The conduction and valence band edge positions are estimated from flat band potential measured at pH = 7 [1].

1.2 Importance of surface study

Understanding the nature of atomic and electronic structures of surfaces is essential in the study of nanoscale photocatalysts [5, 14]. It is not only because nanoscale photocatalysts have high surface-to-volume ratios, but also because different surface orientations and stoichiometries significantly influence the binding energies of reaction intermediates and transition states in the surface reactions. Most importantly, different surface characteristics can lead to significantly different formations of a depletion layer (space charge layer) at the catalyst/electrolyte interface in the process of electrochemical potential equilibration of the photocatalyst surface and water. The depletion layer directly determines the concentrations of dominant charge carriers near the surface, and the \(E_C\) and \(E_V\) positions at the water/photocatalyst interface [15,16]. The \(E_C\) and \(E_V\) positions in an aqueous solution are a critical factor determining the photocatalytic capabilities (generation of electron-hole (\(e-h\)) pairs) and thereby directly influencing the surface reactions for H\(_2\) and O\(_2\) creations in a non-trivial manner [15-17]. Also, the surface effects are significant for nano-sized photocatalysts because band bending (band realignment) at the semiconductor/water interface is known to occur over a distance of 100 Å to several µm from the interface [17-18]. Considering that the CoO nanoparticles used for water splitting are ~ 10 nm in diameter, the nanoparticles could be considered to represent a pure CoO/water interface state without having a bulk-like region in the core. Thus, the experimentally observed upward shift of the band edges of the CoO nanoparticle [1,11] might be related to a specific surface. In order to understand the origin of the improved photocatalytic water splitting activity in a nanoparticle photocatalyst, it is first necessary to have a detailed understanding of the surface atomic and electronic structures of the material as it exists in the aqueous environment.

1.3 Thesis scope and significance

In this thesis, we use first-principles density functional theory (DFT) computations to identify the thermodynamically stable surface structures. Based on the understanding, we also predict morphology of CoO nanoparticles in an aqueous environment. We then investigate the role of the surface state (orientation, adsorbates and stoichiometry) on the band edge positions using explicit solvation calculations. By comparing the band edge positions from explicit solvation calculation with the vacuum reference method
and implicit solvation method, we show that the explicit solvation calculation is essential for accurately modeling the electronic structures of the CoO/water interface. We also discuss the surface state-dependent band edge positions of CoO slabs in terms of the degree of band bending at the CoO/water interface. This work provides a fundamental understanding of why overall water splitting is feasible on the CoO nanoparticles under visible light.

In addition, we extend our DFT computational work to elucidate the mechanism for the spontaneous overall photocatalytic water splitting without external bias or a co-catalyst, but with a very high efficiency. We demonstrate the charge separation for the high photocatalytic efficiency, and compute the energy barriers for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) on the different facets on CoO nanoparticles. Applying the new criteria that HER (OER) can occur if and only if the energy of the photoexcited electrons (holes) is greater than the transition state energy of the rate-limiting step of the half reaction, we predict the predominant reaction sites for HER and OER. We show that these criteria can be met even when the energy levels of the band edges do not span the water redox potentials, contrary to the general belief about photocatalysts.

We believe that our present work provides new insights into the relationships between environmental conditions, surface structure, and band alignment, which may lead to new approaches for optimizing photocatalytic activity in CoO and other oxide photocatalysts. Furthermore, the mechanism suggested in this thesis provides a general framework for understanding previously unexplained experimental observations of overall photocatalytic water splittings on other self-standing photocatalysts which are not predicted to have the required band alignment with respect to the water redox potentials, as well as new criteria for screening and designing novel photocatalysts.
CHAPTER 2. BACKGROUND

2.1 Photocatalytic water splitting

Photoelectrolysis of water using sunlight is very attractive for several reasons. First, this type of solar energy conversion can solve the energy storage problem, since hydrogen can be stored much more easily than either electricity or heat. Second, hydrogen is valuable as a potential fuel and energy carrier [19-20]. It is nonpolluting, renewable, inexhaustible, and very flexible: can be easily converted into other forms of energy (heat via combustion or electricity via fuel cells). Finally, hydrogen is valuable as a basic chemical feedstock used in large quantities for ammonia synthesis and petroleum refining.

Since the current source of hydrogen is primarily steam reforming of natural gas, a new process based on water and sunlight would be a very important development, both environmentally and economically. During photoelectrolysis, optical energy is converted into chemical energy in the form of the free energy of the resultant products. Although decomposition of water into H₂ and O₂ is of the greatest importance, other significant endoergic and exoergic reactions are also possible via photoelectrolysis. Alternatively, in photoelectrochemical systems, optical energy can be converted into electrical rather than chemical energy.

2.2 Photon absorption and band edge positions

A semiconducting material absorbs light through interband absorption ($E_i$ to $E_f$) when the photon energy ($h\nu$) is greater than the band gap energy ($E_g$) of the semiconductor. The photon absorption can excite electrons from occupied states in the valence band to unoccupied states in the conduction band of the semiconductor, which results in the generation of electron-hole pairs ($e^- - h^+$), as schematically illustrated in Figure 2-1(a). The photon absorption and e-h pair generation in semiconducting materials are largely determined by their band structures, and the density of states for the transition.

When the semiconducting material is immersed in water, photogenerated holes can participate in water oxidation at the photo-anode, while photogenerated electrons can work for water reduction reaction at the photo-cathode as summarized in equations 2.1 and 2.2.

1) Photo-anode : \( 2H_2O(l) \rightarrow 2O^{2-} + 4H^+ + 4h^+ \rightarrow O_2(g) + 4H^+ \)  \hspace{1cm} (2.1)

2) Photo-cathode : \( 4H^+ + 4e^- \rightarrow 2H_2(g) \)  \hspace{1cm} (2.2)
Overall water splitting creates stoichiometric H₂ and O₂ (2:1) at the two electrodes; thermodynamically, it requires 1.23 eV per electron transfer to drive water splitting at 25 °C and pH=7.

\[
\text{H}_2\text{O}(l) + 2.46 \text{ eV} = \text{H}_2(g) + \frac{1}{2}\text{O}_2(g)
\] (2.3)

Therefore, the energy difference between the H⁺/H₂ and H₂O/O₂ levels is 1.23 eV as shown in Figure 2-1(b). However, practically it requires additional energy, i.e., overpotential (\(\eta\)), to overcome any kind of reaction barrier for both half reactions (HER and OER), so a photon energy – and thus band gap – of 1.23 eV + \(\eta_{\text{HER}} + \eta_{\text{OER}}\) is needed for an actual photocatalysis. Materials with band gap size corresponding to the visible light spectrum are more highlighted than those with the UV spectrum, because the energy gap size allows the electrons and holes to overcome kinetic barriers in the HER and OER, while capturing a significant portion of the solar spectrum.

**Figure 2-1** (a) Intraband optical absorption between an initial state of energy \(E_i\) in an occupied valence band and a final state at energy \(E_f\) in an empty conduction band, under photon energy (\(\hbar\omega\)). The energy difference between the two band edges (\(E_C\) and \(E_V\)) is the band gap of the above semiconductor (\(E_g\)) [21] (b) \(E_C\) and \(E_V\) positions of a semiconducting photocatalyst relative to water redox potentials, optimal for overall water splitting under irradiation.

In addition to band gap size of a photocatalyst, the \(E_C\) and \(E_V\) positions relative to water reduction and oxidation potential levels are widely accepted primary criteria for determining the photocatalytic capability to evolve H₂ and O₂ from water splitting for a variety of photocatalytic materials (Figure 2-2). This criterion is based on the idea that in order to make it energetically favorable for photogenerated charge carriers to leave the material and induce both the water reduction and oxidation reactions at the surface, the
energy of the electron (or hole) photogenerated in the semiconductor should be greater than the hydrogen evolution potential level for H₂ (or oxygen evolution potential for O₂). Simply, $E_C$ should be more negative relative to H⁺/H₂ level for HER, while $E_V$ be more positive relative to H₂O/O₂ level for OER. If both conditions are satisfied as shown in Figure 2-1(b), photocatalytic overall water splitting is expected to occur in the semiconducting photocatalyst. Among the photocatalytic materials shown in Figure 2-2, GaP, CdS, anatase TiO₂, SiC are expected to conduct overall water splitting under irradiation, considering that both H⁺/H₂ and H₂O/O₂ levels are in their band gap region (between $E_C$ and $E_V$).

![Figure 2-2 Conduction and valence band edge positions of various photocatalysts relative to water redox potentials](image)

2.3 Space charge layer formation at surface

The $E_C$ and $E_V$ positions relative to water redox potential in an aqueous environment are directly determined by the energy band alignment of a semiconductor and water. The band alignment of a semiconductor to the water redox potential is determined by the equilibration of the electrochemical-potential i.e., Fermi level, with the oxidation/reduction potentials of the medium (or adsorbed molecules), despite the variation in the electronic properties by material. Figure 2-3(a) shows a schematic of an energy diagram of an $n$-type semiconductor and an electrolyte. When an $n$-type semiconductor and a redox couple come into contact (Figure 2-3(b)), equilibration of the electrochemical potential is achieved by electron transfer from the $n$-type semiconductor to oxidant. As a result, the Fermi levels are at the same level between
the semiconductor and the electrolyte (water in this case). Hence, the charge density and properties at the surface of the semiconductor deviate from the bulk region. Specifically, the charges are deficient at the surface, which in turn results in upward band bending. This region in which the band bending occurs is normally known as ‘space charge layer’ or ‘depletion layer’. In the case of a p-type semiconductor, electrons normally transfer from the electrolyte to the semiconductor to balance the Fermi levels of the semiconductor and water, which results in downward band bending at the semiconductor/water interface [23]. Therefore, the kinetics and energetics of electron transfer across semiconductor/electrolyte interfaces are determined by the nature of the semiconductor, which in turn characterizes the nature of the space charge layer, and band bending aspects at the surface of a photocatalyst.

Figure 2-3 A schematic of an energy diagram of n-type semiconductor and electrolyte (a) when the semiconductor and electrolyte are separated and (b) when they are in equilibrium after contact [24]. CB, VB, $E_G$ and $E_F$ denote the conduction and valence band edges, the band gap energy, and the Fermi level in the semiconductor. Ox and Red are the redox states in electrolyte, $E_{(\text{redox})}$ is the redox Fermi level.

In addition to the nature of a material itself, surface states and environments also largely affect the formation of space charge layer and the band bending aspect, because the electron transfer across the surface/water interface is affected by the surface characteristics: mostly charge states [14-17]. For example, if an n-type semiconductor has more electrons at the surface (negatively charged surface), more electrons favor moving towards the electrolyte from the surface, in the process of electrochemical potential equilibration, resulting in more severe electron depletion in the space charge layer – thus, more significant upward band bending and more negative $E_C$ and $E_V$ relative to $H^+/H_2$. Accordingly, photocatalysts with same material in the center (bulk region) can have different space charge layer, which can lead the $E_C$ and $E_V$ to position in different levels relative to water redox potentials.

A nano-sized particle smaller than the width of the space charge layer ($d_{sc}$) as shown in Figure 2-4 has the characteristics of a pure surface since it does not have a bulk region in the center, unlike the particle
with \( d > d_{sc} \), where \( d \) is the diameter of the particle. However, the \( E_C \) and \( E_V \) in both cases of \( d > d_{sc} \) and \( d \ll d_{sc} \), are determined by the nature of the space charge layer, which is mainly affected by the electron transfer across the surface and the electrolyte (or other medium). Therefore, the \( E_C \) and \( E_V \) positions in a nano-sized particle would be similar to those larger than \( d_{sc} \) regardless of the particle size, even though the nanoparticle does not show the band bending in the particle due to the absence of a bulk-like region in the center. Accordingly, the \( E_C \) and \( E_V \) of a material reflects the surface states and the nature of space charge layer at the surface, rather than a size effect (whether particles have a bulk-like region or not).

**Figure 2-4** Schematics of energy band diagram in particles with size (a) \( d > d_{sc} \) and (b) \( d \ll d_{sc} \). \( d \) and \( d_{sc} \) denote the particle size and width of space charge layer [25].

### 2.4 Flat band potential measurements

To understand the relative energy levels of the electrolyte and the semiconductor, and the band bending in the semiconductor, it is necessary to introduce the flat-band potential (\( U_{fb} \)), as a critical parameter characterizing the semiconductor electrode.

Changing the voltage of the semiconductor can separate the fermi levels of the semiconductor and redox couple, from equilibrium state in Figure 2-5(a) to close to state in Figure 2-5(b). The electrode potential at which the semiconductor bands are flat (zero space charge in the semiconductor) is the flat-band potential as shown in Figure 2-5(b), measured with respect to a reference electrode, i.e., the normal \( \text{H}^+ / \text{H}_2 \) redox potential (NHE). The flat-band potential informs the difference between the Fermi level of a semiconductor (\( E_F \)) and water redox potential (\( E_F(\text{redox}) \)) in Figure 2-5(b).
Figure 2-5 Schematics of an energy diagram of $n$-type semiconductor and water (a) in equilibrium and (b) under flat band potential ($U_{fb}$) [24].

We can experimentally determine the flat-band potential and describe the nature of the semiconductor–electrolyte interface, using the Mott–Schottky equation [24]:

$$\frac{1}{C^2} = \frac{2}{e\varepsilon \varepsilon_0 A^2 N_D} \left( U - U_{fb} - \frac{k_B T}{e} \right)$$  \hspace{1cm} (2.4)

Here $C$ and $A$ are the interfacial capacitance and area, respectively, $e$ is the electronic charge, $\varepsilon$ is the dielectric constant of the semiconductor, $\varepsilon_0$ is the permittivity of free space, $N_D$ is the number of donors, $U$ is the applied voltage, $k_B$ is Boltzmann’s constant, and $T$ is the absolute temperature. This Mott-Schottky equation is derived from the distribution of electrons in the space charge layer and Gauss’ law, which relates the electric field through the interface to the charge contained within the space charge layer. A plot of $\frac{1}{C^2}$ against $U$ should yield a straight line (Figure 2-6) from which $U_{fb}$ can be determined from the intercept on the $U$ axis. The value of $N_D$ can also be conveniently found from the slope knowing $e$ and $A$. The flat band potentials of CoO micro- and nano-powders measured in an aqueous solution were evaluated as 2.1 and 3.5 eV as shown in Figure 2-6.
Figure 2-6 Mott–Schottky plots for CoO nanocrystals and micropowders according to impedance measurements. The flat-band potentials are obtained from the intercepts of the extrapolated lines [1].

2.5 Three steps of photocatalysis

Catalysis on a semiconducting photocatalyst generally involves three steps as schematically explained in Figure 2-7: (i) solar light absorption, which generates electron-hole pairs if the energy of the incident light is larger than the band gap; (ii) separation of the photogenerated charge carriers and transportation to the surface of the photocatalyst; and (iii) reaction of adsorbed reactants at the surface via use of the transferred photogenerated electrons/holes. Photogenerated holes are used to generate oxygen at the photoanode (\(4h^+ + H_2O(l) \rightarrow O_2(g) + 4H^+\)), while photogenerated electrons generate hydrogen at the photocathode (\(4H^+ + 4e^- \rightarrow 2H_2(g)\)). Consequently, the two half reactions lead to stoichiometric generation of hydrogen and oxygen from water (\(2H_2O(l) \rightarrow O_2(g) + 2H_2(g)\)).

For spontaneous photocatalytic overall water splitting under irradiation without the help of external bias (driving potential), the charge separation and surface reactions as well as the light absorption with optimal band edge positions, should be completed by the photon energy (\(h\omega\)) absorbed by a semiconductor.
Figure 2-7 Schematic figure explaining three step mechanism of photocatalysis for hydrogen and oxygen evolution on nanoscale self-standing photocatalysts [26].

2.6 Electrochemical cell type of photocatalyst

Figure 2-8 shows the general photo-electrochemical cell (PEC), which is designed for realizing the photocatalytic water splitting using a semiconducting photocatalyst. A photocatalytically active semiconductor electrode (photo-anode) and a metal counter electrode (photo-cathode) are separated with hydronium ion permeable membrane (‘Frit’ in Figure 2-8). The interaction of light with the semiconductor electrode produces electron–hole pairs, of which the holes oxidize water at the semiconductor electrode surface to form O₂, and the electrons migrate to the counter electrode to reduce water to form H₂.

The PEC-type system normally shows a higher conversion efficiency compared to a single-material system; however, it is not economical because external bias is needed for macroscale charge separation between the two electrodes. Therefore, in recent years, nanostructured materials have emerged as an essential component of photocatalysts, because nanostructures can be more economical for photocatalytic water splitting as explained in the next section.
Figure 2-8 Photoelectrochemical cells with semiconductor electrode [27].

2.7 Nano-sized self-standing photocatalyst

In order to make photocatalytic water splitting economically feasible, it is crucial to decrease both the material cost and the energetic cost (i.e., overpotential) for the two half reactions (HER and OER). Recently, nanostructured materials have emerged as an essential component of photocatalysts. In particular, particulate or colloidal photocatalysts have many advantages, such as simple and relatively inexpensive fabrication processes and the ability to be used on flexible substrates. In addition, the reduction of particle size generates various crystalline facets, as well as a high specific surface area, leading to a large number of active sites. The decreased length scale also results in shorter carrier diffusion lengths, thereby increasing the probability that electrons and holes will reach the photocatalyst/water interface, where they can participate in the HER and OER, respectively. Furthermore, the reduction of particle size can also induce quantum confinement effects, leading to an increased band gap, which may be used to optimize the band edge positions relative to the water redox potentials, further increasing efficiency. However, the benefits of size reduction may be cancelled out by an increase in electron-hole recombination due to the confined space of the nanoparticle as well as the difficulty of energy band bending (flat band in the entire nanoparticle as shown in Figure 2-4), which would significantly reduce efficiency. Therefore, charge separation is a crucial step for high conversion efficiency with a nanoparticle photocatalyst. Thus, it is difficult to imagine economical nanoparticle photocatalysts inducing overall water splitting without the application of external energy and/or a co-catalyst.
2.8 HER and OER co-catalysts

Metal or metal oxide co-catalysts, therefore, are often added to self-standing nanoparticle photocatalysts in order to separate the photogenerated electrons and holes (step (ii) in the photocatalysis), as well as to promote the HER and OER reactions by reducing the reaction barriers (step (iii) in the photocatalysis), as schematically explained in Figure 2-7. In general, noble metals including Pt, Pd, Rh and Ni, Co, Cu are known as good HER co-catalysts, while metal oxides such as IrO\textsubscript{2}, RuO\textsubscript{2}, Co\textsubscript{3}O\textsubscript{4}, and NiO are known as good OER co-catalysts. This is because metals normally have higher electron affinity (with higher work function) than metal oxides, which in turn strongly attracts the photogenerated electron and separates the photogenerated charges. It is also because metals have lower HER overpotentials, while metal oxides have lower OER overpotential, showing high activities for the half reactions [28, 29], respectively.

2.9 Model system

Contrary to the general belief about nanostructured photocatalyst, some single-material nanoparticles including \(\gamma\)-Ga\textsubscript{2}O\textsubscript{3} [30], Cu\textsubscript{2}O [31], ZrO\textsubscript{2} [32], KTaO\textsubscript{3} [33], Zn\textsubscript{2}GeO\textsubscript{4} [34-35], p-GO:N/n-GO:N [36], BiVO\textsubscript{4} [37-38] and CoO [1], showed overall water splitting, even without a co-catalyst or an externally applied bias. However, we still do not understand how the overall water splitting could occur on the monolithic self-standing photocatalysts, without a co-catalyst or an external bias.

We selected CoO nanoparticles as a model system because CoO nanoparticles smaller than 10 nm showed highest photocatalytic efficiency among the single-material photocatalysts inducing overall water splitting in neutral water. The CoO nanoparticles have an optimal band gap for visible light absorption (2.6 eV); therefore, it is expected that the CoO nanoparticles can absorb large fraction of solar spectrum. Also, we do not need to worry about photo-degradation by UV light, since CoO nanoparticles are photocatalytically active under visible light spectrum. CoO nanoparticles are also very attractive for materials scientists because they consist of earth-abundant element, Co, cheaper than noble metals.
CHAPTER 3. METHODS

3.1 Structure preparation

3.1.1 Bulk CoO

Bulk CoO crystallizes in the rock salt structure (Fm\(\overline{3}m\) space group), with both Co and O atoms in octahedral environments [39]. Experimentally, ground-state CoO exhibits type-II antiferromagnetic (AFM-II) spin ordering, in which the magnetic moments of the Co\(^{2+}\) ions are aligned in parallel within each (111) plane, with antiparallel ordering of adjacent (111) planes [40-42]. To determine the ground state magnetic ordering and electronic structures of bulk CoO within DFT, we use a 2 \(\times\) 2 \(\times\) 1 supercell containing 32 atoms. To address the strongly correlated and localized 3d shell of Co, we employ the DFT + Hubbard \(U\) (DFT + \(U\)) approach within spin-polarized density functional theory. DFT + \(U\) calculations are performed using VASP [43-44] with projected augmented wave (PAW) pseudopotentials from the VASP database and the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) to describe the exchange-correlation effects [45]. An energy cutoff of 800 eV and a 6 \(\times\) 6 \(\times\) 6 Monkhorst-Pack k-point mesh are used. Atom positions are relaxed until all forces are less than 0.005 eV/Å.

The choice of \(U_{\text{eff}}\) (\(U_{\text{eff}} = U - J\)) significantly affects the magnitude of the band gap, the equilibrium lattice constant, and the relative energies of magnetic configurations. We find that varying \(U_{\text{eff}}\) from 0 eV to 6 eV changes the lattice constant of rock salt AFM-II CoO from 4.17 to 4.27 Å, in particular, \(U_{\text{eff}} = 4.1\) eV gives a lattice constant of 4.26 Å (Figure 3-1), in very good agreement with the experimental value of 4.262 Å [46-49]. This choice of \(U_{\text{eff}}\) also provides good agreement with the experimental measurements of the CoO band gap, magnetic configuration, and magnetic moments, as shown in Figure 3-1 and Table 3-1.

![Figure 3-1 Lattice constant, band gap, and magnetic moment per Co atom, of bulk CoO, with respect to \(U_{\text{eff}}\).](image)
Table 3-1 Lattice constant, band gap, magnetic moment per Co atom, of bulk AFM-II CoO, computed with various $U_{\text{eff}}$ in the present study.

<table>
<thead>
<tr>
<th></th>
<th>a=b=c (Å)</th>
<th>$E_g$ (eV)</th>
<th>Magnetic moment (µB)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.</td>
<td>4.26</td>
<td>2.4-2.6</td>
<td>2.38-2.98*</td>
<td>[42,46,49,50]</td>
</tr>
<tr>
<td>AFM-II – no $U_{\text{eff}}$</td>
<td>4.17</td>
<td>0.22</td>
<td>2.45</td>
<td>Present</td>
</tr>
<tr>
<td>AFM-II – $U_{\text{eff}} = 1$</td>
<td>4.19</td>
<td>0.33</td>
<td>2.56</td>
<td>Present</td>
</tr>
<tr>
<td>AFM-II – $U_{\text{eff}} = 2$</td>
<td>4.22</td>
<td>1.08</td>
<td>2.62</td>
<td>Present</td>
</tr>
<tr>
<td>AFM-II – $U_{\text{eff}} = 3$</td>
<td>4.24</td>
<td>1.73</td>
<td>2.68</td>
<td>Present</td>
</tr>
<tr>
<td>AFM-II – $U_{\text{eff}} = 4.1$</td>
<td>4.26</td>
<td>2.30</td>
<td>2.77</td>
<td>Present</td>
</tr>
<tr>
<td>AFM-II – $U_{\text{eff}} = 5$</td>
<td>4.26</td>
<td>2.66</td>
<td>2.76</td>
<td>Present</td>
</tr>
<tr>
<td>AFM-II – $U_{\text{eff}} = 6$</td>
<td>4.27</td>
<td>1.71</td>
<td>2.79</td>
<td>Present</td>
</tr>
<tr>
<td>AFM-II – $U_{\text{eff}} = 4.1$</td>
<td>4.27</td>
<td>2.30</td>
<td>2.67</td>
<td>[46]</td>
</tr>
<tr>
<td>AFM-II – $U_{\text{eff}} = 4$</td>
<td>4.27</td>
<td>2.68</td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>AFM-II – $U_{\text{eff}} = 3.5$</td>
<td>4.25</td>
<td></td>
<td></td>
<td>[52]</td>
</tr>
<tr>
<td>AFM-II – no $U_{\text{eff}}$</td>
<td>4.22</td>
<td>0.8</td>
<td>2.42</td>
<td>[53]</td>
</tr>
</tbody>
</table>

To determine the ground state magnetic configuration, we considered structures with up and down spins on Co ions in alternating planes along (001), (110), and (111) directions, corresponding to AFM-A, -C, and –G (type-II) ordering, as well as a structure with two up-spin planes and two down-spin planes along (002) (AFM-A). The calculated magnetic moments and relative total energies are summarized in Table 3-2. As the table shows, we find that bulk CoO has the lowest energy in the AFM-II (111) phase, in agreement with previous work [40,41,46]. In addition, the magnetic moment of this phase is ~ 3 µB per Co, in good agreement with experiment and theory [46], and the band gap is 2.3 eV (Table 3-2 and Figure 3-2), in reasonable agreement with the experimental measurements (2.4-2.6 eV [1,10,54]), further motivating this choice of $U_{\text{eff}}$.

Table 3-2 Magnetic configurations of bulk CoO and their band gap, magnetic moment per Co atom, and energy difference between AFM and non-magnetic phases.

<table>
<thead>
<tr>
<th></th>
<th>a=b=c (Å)</th>
<th>$E_g$ (eV)</th>
<th>Magnetic moment (µB)</th>
<th>$\Delta E_{\text{AFM} – \text{non-mag}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.</td>
<td>4.26</td>
<td>2.4-2.6</td>
<td>2.38-2.98*</td>
<td></td>
</tr>
<tr>
<td>Non-magnetic</td>
<td>4.16</td>
<td>2.4-2.6</td>
<td></td>
<td>0.00</td>
</tr>
<tr>
<td>AFM-A (1 × 1) (001)</td>
<td>4.26</td>
<td>0.37</td>
<td>2.78</td>
<td>-25.30</td>
</tr>
<tr>
<td>AFM-C (110)</td>
<td>4.21</td>
<td>0.70</td>
<td>2.73</td>
<td>-25.97</td>
</tr>
<tr>
<td>AFM-G (111) (type-II)</td>
<td>4.26</td>
<td>2.30</td>
<td>2.77</td>
<td>-29.02</td>
</tr>
<tr>
<td>AFM-A (2 × 2) (002)</td>
<td>4.21</td>
<td>0.63</td>
<td>2.75</td>
<td>-26.31</td>
</tr>
</tbody>
</table>
3.1.2 CoO surfaces in vacuum

To study the stability of different surface configurations and stoichiometries, we first model the (100) and (111) surfaces of CoO using symmetric supercells in vacuum. We consider only these two orientations based on the experimental data indicating that they are the main surface facets present in both nanoparticles and micropowders [55-57]. The structural and electronic properties of the CoO(100) surfaces are found to converge for slabs composed of 7 atomic layers, with a $(2 \times 2)$ in-plane unit cell. The O- and Co-terminated CoO(111) surface properties are found to converge for slabs composed of 13 atomic layers, with a $(2 \times 2)$ in-plane unit cell. In all cases, a vacuum of $\sim 15 \text{ Å}$ separates periodic copies of the slab perpendicular to the surface. The atoms in the central three (five) atomic planes are fixed in the bulk CoO positions for CoO(100) (for CoO(111) surfaces), while all other atoms are allowed to fully relax. A $6 \times 6 \times 1$ Monkhorst-Pack k-point mesh is used. A type-II magnetic configuration is used in all slab structures, as in Refs. 46, 52.

3.2 Oxygen vacancy formation on CoO surfaces

We consider CoO(100) and CoO(111) slabs with neutral oxygen vacancies ($V^0_O$). Oxygen atoms are removed to both sides of the relaxed bare slabs. The surface oxygen vacancy concentration varies from 1/8 to 1. For the calculation of the CoO(111) surface, a double-sized slab along the $x$-axis was used in order to 1) match the number of surface atoms on the CoO(100) slab, and 2) examine a wider range of surface oxygen vacancy concentrations.

Figure 3-2 Total density of states (DOS) of bulk CoO of AFM-II computed with $U_{\text{eff}} = 4.1 \text{ eV}$. $E_V$ is the energy of the valence band edge.
3.3 H, O, OH adsorption on CoO surfaces

Potential adsorbates (e.g., H, O, OH) that may be present in an aqueous environment are added to both sides of the relaxed bare slabs (CoO(100), CoO(111) and Co/CoO(111)) to obtain the initial starting positions. The adsorbates are initially positioned at ~2 Å distant from the surface and relaxed to find the minimum energy adsorption site and geometry. All adsorbates were found to prefer the on-top site for CoO(100) and the bridge site for CoO(111), consistent with Ref. 52.

3.4 Band edge positions of CoO

3.4.1 \(E_C\) and \(E_V\) in vacuum

In the solid state physics, the zero reference point of the energy scale is vacuum. But, it is the standard redox potential of the hydrogen ion-hydrogen (H\(^+\)/H\(_2\)) redox couple in the electrochemistry. It has been shown [59] that these scales are related in which the effective work function (or Fermi level) for the standard H\(^+\)/H\(_2\) redox couple at equilibrium is -4.5 eV with respect to vacuum. Hence, using this scheme, the energy levels corresponding to a redox couple can be related to the energy levels of the \(E_C\) and \(E_V\) of the semiconductor.

To compute the \(E_C\) and \(E_V\) for CoO slabs with different surface configurations in vacuum, the vacuum level in each CoO slab/vacuum supercell is found by obtaining the local potential energy versus position along the axis perpendicular to the slab surface as shown in Figure 3-3 for an example. We first computed the \(E_V\) relative to the vacuum level \((E_{\text{vac}})\) for the slabs in vacuum, then determined \(E_C\) by adding the experimental band gap \((E_g^{\text{expt}})\) to the computed \(E_V\). The reason for the selection of this method to calculate EC of semiconductor is explained in sections 4.3.4.1 and 4.3.6.
Figure 3-3 An example of local potential energy versus position along the axis perpendicular to the slab surface in CoO slab. $E_{\text{vac}}$ is vacuum level for the slab.

3.4.2 $E_C$ and $E_V$ in an aqueous environment

3.4.2.1 Three step calculations for explicit solvation method

To predict the band edge positions of CoO surfaces in an aqueous solution, we use an explicit solvation calculation approach similar to the three-step method introduced in Ref. 60, which is shown schematically in Figure 3-4. The approach directly investigates the position of the conduction band edge of a material relative to the water reduction potential ($\text{H}^+/$H$_2$) level, which is determined by three energy values of (1) bulk semiconductor (or insulator), (2) bulk liquid water, and (3) the material/water interface; (1) energy difference between the $E_C$ and the average Hartree potential of bulk semiconductor ($E_C^{\text{S.C.(bulk)}} - H^{\text{S.C.(bulk)}}$), (2) energy difference between the $\text{H}^+/$H$_2$ level and the average Hartree potential of bulk liquid water ($A^{\text{water (bulk)}} - H^{\text{water (bulk)}}$) and (3) average Hartree potential difference in the semiconductor and water regions at the interface ($H^{\text{S.C.(interface)}} - H^{\text{water (interface)}}$).
Figure 3-4 Left: Schematic of the three step approach for determining the position of the conduction band edge \((E_C)\) of a semiconductor relative to the water reduction potential \((H^+ / H_2)\) \([60]\). Right: Equation for CoO.

### 3.4.2.2 Bulk liquid water and its \(H^+ / H_2\) level

To find the \(H^+ / H_2\) acceptor level (LUMO of bulk liquid water) relative to the Hartree potential in bulk liquid water, we first perform classical molecular dynamics (MD) simulations at room temperature using the LAMMPS code \([61]\) to make bulk liquid water. The TIP4P/2005 potential \([62]\) was employed to describe the atomic configuration and the interaction between water molecules. The simulation cell consists of 140 \(H_2O\) (~11 × 11 × 27 Å\(^3\)) to mimic the density of liquid water (1g/cm\(^3\)) and is equilibrated within the NVT ensemble for 1000 ps. Using the atomic configuration obtained from the classical MD calculation, the density of states (DOS) of bulk liquid water was then calculated at the \(\Gamma\) \(k\)-point using DFT.

The \(H^+ / H_2\) acceptor level is determined using the approach described in Ref. 60. One of the 140 \(H_2O\) molecules in the MD-equilibrated bulk liquid water system is substituted by \(H_3O^+\), then the atomic configuration is optimized using DFT. Using the DFT-optimized \(H_3O^+\) containing liquid water structure for a static DFT calculation, the energy level of the \(H_3O^+\) ion in water \(i.e.,\) the acceptor level of water is obtained.

### 3.4.2.3 Potential drop at CoO/water interface

Initial CoO/water interfaces are constructed by combining the relaxed CoO slabs with the optimized bulk water into supercells with a total length of 45-50 Å in the direction perpendicular to the interface. The CoO slabs are 15-18 Å thick, depending on the orientation and the slab thickness determined in vacuum, and the water region is 27-30 Å thick. The Hartree potentials of the combined CoO/water interface systems are determined using static DFT calculations without spin polarization and Hubbard \(U\) correction of cobalt.
The reason for the ignorance of the spin polarization and Hubbard $U$ correction of Co atoms is explained in sections 4.1.6.2 and 4.1.6.3.

### 3.5 HER and OER overpotentials

To begin, we determine the relative HER activities of the CoO surfaces by determining the free energy change for H adsorption ($\Delta G_{\text{H}*}$), which has been shown to be a good descriptor for the HER exchange current density ($j_0$) for a wide variety of surfaces [63-64]. The value of $\Delta G_{\text{H}*}$ can be computed by modeling the possible intermediates formed during the hydrogen adsorption-reduction-desorption processes at the cathode, given by the $2\text{H}^+ + 2e^- \rightarrow \text{H}^* + \text{H}^+ + e^- \rightarrow \text{H}_2$, where the * represents an active surface site. Using this approach [28,63-65], both $\Delta G_{\text{H}*}$ values and calculated HER activity trends have been shown to agree well with experimental results [66].

According to the Sabatier principle [67-68], a good HER catalyst should form a sufficiently strong bond with adsorbed H* to facilitate the proton-electron-transfer process, yet be weak enough for facile bond breaking and release of H$_2$ gas. We use the convention that negative $\Delta G_{\text{H}*}$ indicates strong binding of hydrogen atoms to the surface, which blocks potential active sites and retards hydrogen generation, while positive $\Delta G_{\text{H}*}$ indicates weak bonding of hydrogen atoms to the surface, which fails to stabilize intermediates and prevents any reaction from taking place. Thus, the highest HER activity is given by $|\Delta G_{\text{H}*}|$ close to 0, i.e., at the summit of the volcano plot of $j_0$ versus $\Delta G_{\text{H}*}$, as shown in Figure 3-5 [28].

![Figure 3-5](image_url)

**Figure 3-5** Experimentally measured exchange current, log($j_0$), for hydrogen evolution over different metal surfaces plotted as a function of the calculated hydrogen chemisorption energy per atom, $\Delta G_{\text{H}*}$ [28].
Like HER, the OER overpotential of a material can be estimated based on the binding energies of the intermediates on the surface relative to H₂O and H₂ in the gas phase. The proposed OER mechanism at photo-anode consists of four consecutive proton and electron transfer steps with the intermediates OH*, O*, OOH* and OO*(O₂) as suggested in Ref. 69. The reaction could be written as [70]:

\[
2\text{H}_2\text{O} \rightarrow \text{HO}^* + \text{H}_2\text{O} + \text{H}^+ + e^- \quad ; \Delta G_{\text{OH}^*} \quad (3.2.a)
\]

\[
\rightarrow \text{O}^* + \text{H}_2\text{O} + 2\text{H}^+ + 2e^- \quad ; \Delta G_{\text{O}^*} \quad (3.2.b)
\]

\[
\rightarrow \text{HO}^* + 3\text{H}^+ + 3e^- \quad ; \Delta G_{\text{OOH}^*} \quad (3.2.c)
\]

\[
\rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \quad (3.2.d)
\]

The largest difference in the free energy change of the intermediates along the reaction path, i.e., max[ΔG_{OH*}, ΔG_{O*}, ΔG_{OOH*}] [29], is taken to be the theoretical OER overpotential (η^{OER}). Previous work has shown that there exists a volcano relationship between the OER overpotential (−η^{OER}) and the descriptor ΔG_{O*}^0 − ΔG_{OH*}^0 on oxide surfaces [29,70,71], as shown in Figure 3-6.
Figure 3-6 Activity trends towards oxygen evolution, for rutile, anatase, Co$_3$O$_4$, Mn$_x$O$_y$ oxides. The negative values of theoretical overpotential were plotted against the standard free energy of $\Delta G_O^{0} - \Delta G_{OH}^{0}$. step [29].

Free energy changes for the intermediates at $P_{H_2} = 1$ bar, were calculated using the approach reported in Ref. 70, where

$$\Delta G(U, \text{pH}, T) = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH},$$

(3.3)

where $\Delta E$ is the reaction energy determined from DFT, $\Delta ZPE$ is the difference in zero-point energies due to the reaction between the adsorbed and the gas phase by setting $H_2O$ and $H_2$ in the gas phase as reference states [70]. $\Delta ZPE$ of various surface are calculated using DFT calculations. $\Delta S$ is the change in entropy, computed using DFT calculations of the vibrational frequencies and standard tables for gas phase molecules, $\Delta G_U = -eU$ is the free energy change due to electrode potential $U$, and $\Delta G_{pH} = kT \cdot ln[H^+] = -kT \cdot \ln 10 \cdot \text{pH}$ is the free energy change due to change in pH. All values of $\Delta G$ are computed at $T = 298$ K, and pH = 0. Additional details and computed values of $\Delta ZPE$ and $T\Delta S$ are reported in Tables 3-3 and 3-4.

Table 3-3 Zero point energies (ZPE), entropies and $\Delta ZPE - T\Delta S$ of CoO(111) and CoO(100) calculated with H, O, OH adsorption at 298 K. All vibrational frequencies are calculated under normal mode. The notation of surface configurations is the same as the one in the main manuscript. The unit is eV/adsorbate.

<table>
<thead>
<tr>
<th></th>
<th>ZPE</th>
<th>TS</th>
<th>ZPE-TS</th>
<th>$\Delta ZPE - T\Delta S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O(l)$ [69]</td>
<td>0.567</td>
<td>0.670</td>
<td>-0.103</td>
<td>-</td>
</tr>
<tr>
<td>$H_2(g)$ [69]</td>
<td>0.264</td>
<td>0.410</td>
<td>-0.146</td>
<td>-</td>
</tr>
<tr>
<td>OH*(1/4)-CoO(111)</td>
<td>0.258</td>
<td>-0.051</td>
<td>0.309</td>
<td>0.3493</td>
</tr>
<tr>
<td>OH*(1)-CoO(111)</td>
<td>0.245</td>
<td>-0.050</td>
<td>0.295</td>
<td>0.3345</td>
</tr>
<tr>
<td>H*(1/4)-CoO(111)</td>
<td>0.057</td>
<td>-0.012</td>
<td>0.070</td>
<td>0.13</td>
</tr>
<tr>
<td>H*(1)-CoO(111)</td>
<td>0.058</td>
<td>-0.013</td>
<td>0.072</td>
<td>0.132</td>
</tr>
<tr>
<td>O*(1/4)-CoO(111)</td>
<td>0.022</td>
<td>0.012</td>
<td>0.011</td>
<td>-0.009</td>
</tr>
<tr>
<td>O*(1)-CoO(111)</td>
<td>0.023</td>
<td>0.011</td>
<td>0.013</td>
<td>-0.007</td>
</tr>
<tr>
<td>H*(1/2)-OH*(1/2)-CoO(111)</td>
<td>0.152</td>
<td>0.038</td>
<td>0.189</td>
<td>0.241</td>
</tr>
<tr>
<td>H*(1/4)-CoO(100)</td>
<td>0.113</td>
<td>-0.030</td>
<td>0.143</td>
<td>0.203</td>
</tr>
<tr>
<td>H*(1)-CoO(100)</td>
<td>0.112</td>
<td>0.030</td>
<td>0.143</td>
<td>0.203</td>
</tr>
</tbody>
</table>
Table 3-4 \( \Delta ZPE - T\Delta S \) used in the calculations of the free energy change throughout the paper. For OOH-adsorbed surface (OOH*), values of O* and OH* are summed.

<table>
<thead>
<tr>
<th>Surface orientation</th>
<th>( \Delta ZPE - T\Delta S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO(111)</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.131</td>
</tr>
<tr>
<td>O</td>
<td>-0.008</td>
</tr>
<tr>
<td>OH</td>
<td>0.342</td>
</tr>
<tr>
<td>OOOH</td>
<td>0.334</td>
</tr>
<tr>
<td>CoO(100)</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.203</td>
</tr>
<tr>
<td>O</td>
<td>0.035</td>
</tr>
<tr>
<td>OH</td>
<td>0.304</td>
</tr>
<tr>
<td>OOOH</td>
<td>0.339</td>
</tr>
</tbody>
</table>
CHAPTER 4. RESULTS AND DISCUSSIONS

4.1 Photocatalytic overall water splitting on CoO nanoparticles: Thermodynamic understanding of light absorption by CoO

4.1.1 Choice of $U_{\text{eff}}$ for bulk CoO

To determine the appropriate value of $U_{\text{eff}}$ for the CoO system, we investigated three different properties of bulk rock salt AFM-II CoO with respect to $U_{\text{eff}}$: lattice constant, band gap and magnetic moments of the Co atoms. The results are summarized in Figure 3-1 and Table 3-1. Lattice constant and magnetic moments of Co atoms gradually increase with increasing $U_{\text{eff}}$, and they slow down the increment and starts convergence at around $U_{\text{eff}} = 4.1$ eV. Lattice constant at $U_{\text{eff}} = 4.1$ eV is closest to the experimental value. 4.262 Å, and magnetic moments greater than $U_{\text{eff}} = 4.1$ eV are close to $3\mu_{\text{B}}$ [46]. The band gap of bulk CoO also increases with increasing $U_{\text{eff}}$, but it abruptly decreases after $U_{\text{eff}} = 5$ eV. In $4.3 \leq U_{\text{eff}} \leq 4.8$ eV, the band gap of bulk CoO is in the experimentally measured values, 2.4–2.6 eV. As reported in other results [46-51], we employed $U_{\text{eff}} = 4.1$ eV in this study because of reasonable lattice constant, band gap and magnetic moments of the Co atoms compared to the experimental values.

Table 3-2 summarizes the calculated lattice constant, band gap, magnetic moments of Co atoms and total energies of bulk CoO of several antiferromagnetic configurations computed with $U_{\text{eff}} = 4.1$ eV. Bulk CoO has the lowest energy with the AFM-II (AFM-G) phase, which has both lattice constant and band gap close to the experimental observations. Figure 3-2 shows the total density of states (DOS) of the bulk CoO AFM-II phase computed with $U_{\text{eff}} = 4.1$ eV. The DOS of the up and down spins exhibits the same aspects, indicative of the antiferromagnetic phase and shows a band gap of 2.3 eV.

4.1.2 CoO surface configuration

Surface effects are significant for nano-sized photocatalysts not only because of large surface-to-volume ratios, but also because nanoparticles represent a pure surface state (especially, space charge layer) without having a bulk-like region in the core. The different surface characteristics can lead to significantly different $E_{\text{C}}$ and $E_{\text{V}}$ positions in an aqueous solution, influencing light absorption of a semiconducting photocatalyst (generation of electron-hole ($e$-$h$) pairs) and thereby affecting the surface reactions for H2 and O2. Therefore, understanding the surface nature of nanocrystals as a function of conditions is crucial in order to understand and predict their photocatalytic activity.

The CoO(100) surface orientation is expected to be favorable due to charge balance and the close-packed nature of the non-polar planes normal to the surface [72]. Nevertheless, experimentally, both the
CoO(111) and CoO(100) surfaces have been observed. In particular, CoO thin films generated via oxidation of a Co(0001) substrate or deposition on a Au(111) substrate exhibit (111) surface orientations [73-74]. Moreover, different ratios of (100) or (111) facets have been observed on CoO particles depending on particle size [55], with larger particles on the order of several hundreds of nanometers in size exhibiting octahedral shapes with only (111) surface orientation, while smaller particles (~ 10 nm) were found to have spherical shapes with multiple facets. Therefore, we focus on CoO(100) and Co- and O-terminated CoO(111) slabs in this study.

We first consider CoO surfaces in contact with vacuum, which will be used as a starting point for CoO/water interfaces. Our calculations confirm a much lower surface Gibbs free energy for ideal CoO(100) \( (\gamma_{\text{CoO(100)}} = 0.05) \) compared to ideal CoO(111) \( (\gamma_{\text{CoO(111)}^{\text{Co-terminated}}} = 0.20, \gamma_{\text{CoO(111)}^{\text{O-terminated}}} = 0.21) \) surfaces in vacuum. In agreement with LEED theory and experiment in vacuum [75], our results show that the atomic structure and projected density of states (pDOS) of the CoO(100) surface do not differ significantly from bulk CoO. Therefore, the surface properties are essentially the same as those of the bulk phase as shown in Figure 4-1. We also find that the Co-terminated CoO(111) surface is a slightly more stable than the O-terminated one, in good agreement with the experimental observations that the CoO(111) surface is Co-rich [73]. Hence, we consider only the Co-terminated CoO(111) surface, referred to simply as the CoO(111) surface, in the remainder of this paper.

**Figure 4-1** Projected density of states (pDOS) of each layer in a symmetric 7 atomic layer thick CoO(100) slab with respect to the Fermi level, \( E_F \). Blue, purple, green, gray, and orange solid lines indicate Co \( s \), Co \( p \), Co \( d \), O \( s \), and O \( p \) orbitals, respectively. The label 1 indicates the surface layer.
Nanocrystalline cobalt oxide has been observed experimentally to prefer a stoichiometry close to CoO rather than Co$_3$O$_4$ [76]. This oxidation state suggests that oxygen vacancies are more likely to form than oxygen interstitials in cobalt oxide nanocrystals in the process of manufacturing. We note that although it is commonly accepted that oxygen interstitials (or cobalt deficiencies) are the main source of the $p$-type semiconducting behavior in CoO [77-78], oxygen vacancies are potentially able to be created under realistic water splitting condition, i.e., relatively oxygen-lean condition. Therefore, oxygen vacancies are beginning to be regarded as important point defects in nanocrystalline CoO. For example, the formation of oxygen vacancies was recently shown to alter the activities of CoO nanoparticles for methanol steam reforming by changing the Co$^0$/Co$^{2+}$ ratio [79-80], and oxygen vacancies have been implicated in tuning the performance and sustainability of Li-air batteries with CoO bifunctional cathode catalysts [81].

4.1.3 Oxygen vacancy formation energy in CoO surfaces

We investigate the stability of CoO(100) and CoO(111) surfaces by computing the formation energy of neutral oxygen vacancies ($E_f^{V_O}$) only in the topmost atomic layer, for simplicity [82-85].

$$E_f^{V_O} = E_{tot}^{V_O} - E_{tot}^{\text{perfect}} + \sum n_O \mu_O, \quad (4.1)$$

Where $E_{tot}^{V_O}$ is the total energy of a relaxed supercell containing the neutral oxygen vacancy, and $E_{tot}^{\text{perfect}}$ is the total energy for the perfect crystal using an equivalent supercell. The integer $n_O$ indicates the number of O atoms that have been removed from the supercell to form the oxygen vacancy, and the $\mu_O$ is the corresponding oxygen chemical potential. Here, we assume that the slab structure is in equilibrium with bulk CoO; therefore, the chemical potentials of Co and O again satisfy equation 4.2.

$$\mu_{\text{Co}} + \mu_O = \mu_{\text{CoO}}^{\text{bulk}}, \quad (4.2)$$

The chemical potential of oxygen ($\mu_O$) is determined by O$_2$ in the gas phase reservoir through

$$\mu_O = \frac{1}{2}\mu_{\text{O}_2(g)}, \quad (4.3)$$

and the chemical potential of gas phase O$_2$ is given by

$$\mu_{\text{O}_2(g)} = E_{\text{O}_2(g)}^{\text{DFT}} + E_{\text{O}_2(g)}^{\text{ZPE}} + \Delta G_{\text{O}_2(g)}^0(T) + k_BT \ln \left( \frac{p_{\text{O}_2}}{p_O^0} \right), \quad (4.4)$$

where $E_{\text{O}_2(g)}^{\text{DFT}}$ is the DFT-calculated total energy of an isolated O$_2$ molecule and $E_{\text{O}_2(g)}^{\text{ZPE}}$ is the zero-point energy correction, $E_{\text{O}_2(g)}^{\text{ZPE}} = \frac{1}{2} \hbar \omega_{\text{O}_2(g)}$. These two terms represent the Gibbs free energy of O$_2$ at 0 K. The
third term in equation 4.4, \( \Delta G_{O_2(g)}^0(T) = G_{O_2(g)}(T, p^0) - G_{O_2(g)}(0 \text{ K}, p^0) \), is obtained from thermodynamic tables [86]. The standard pressure, \( p^0 \), is 1 atm and \( T = 298.15 \) °C, \( k_B \) is the Boltzmann constant. The change of oxygen chemical potential (\( \Delta \mu_O \)) is referenced to the half of the total energies of isolated \( O_2 \) molecules at 0 K, i.e., \( \Delta \mu_O = \mu_O - \frac{1}{2}(E_{O_2}^{\text{DFT}} + E_{O_2}^{\text{ZPE}}) \). This definition is consistent with that used in Ref. 52.

Figure 4-2 shows the oxygen vacancy formation energies on CoO(100) and CoO(111) slabs with different oxygen vacancy concentrations (\( V_O = 1/8, 1/4, 3/8, 1/2, 3/4, \) and 1) in the surface atomic plane as a function of \( \Delta \mu_O \). Here, we assume that the slab structure is in equilibrium with bulk CoO; therefore, the chemical potentials of Co and O again satisfy equation 4.2, and the oxygen vacancy formation energy is computed using equations 4.1 and 4.2. As shown in Figure 4-2, the CoO(100) surface remains stoichiometric in a wide range of oxygen chemical potential (\( \Delta \mu_O \geq -1.3 \)) around realistic water splitting condition. On the other hand, it is thermodynamically favorable to have a full layer of oxygen vacancies on the CoO(111) surface, i.e., a layer of Co metal on the CoO(111) surface, in oxygen-lean conditions (\( \Delta \mu_O \leq -0.55 \)). This is consistent with recent experiments demonstrating the generation of Co/CoO(111) in oxygen-lean conditions [87]. Thus, we predict that Co/CoO(111) and/or defect-free CoO(100) are the most likely surfaces that will be present on CoO nanoparticles under conditions relevant to water splitting (-1 \( \leq \Delta \mu_O \leq 0 \)) as shaded with green bar in Figure 4-2.

![Figure 4-2](image_url) Variation of oxygen vacancy formation energy on CoO(100) and CoO(111) surfaces with respect to \( \Delta \mu_O \) for various surface oxygen vacancy concentrations, \( V_O = 1/8, 1/4, 3/8, 1/2, 3/4, 1 \). The lines
of CoO(111)-$V_0$=1/2 and $-V_0$=3/4 are out of range, they are much larger than the other lines in the figure. Values are normalized by the total number of unit cells.

4.1.4 Surface free energy of CoO surfaces

In addition to oxygen vacancies, in a realistic water environment, various molecules dissociated from water, i.e., H, O, and OH, can be adsorbed on the surfaces of photocatalysts, potentially resulting in varied thermodynamic stability of the surfaces. We therefore consider surfaces formed by the adsorption of these species on the Co/CoO(111), CoO(100), and CoO(111) surfaces. The surface free energy is given by

$$\gamma = \frac{1}{2A} \left[ G_{\text{slab}}^{\text{slab}} - N_{\text{Co}} g_{\text{CoO}}^{\text{bulk}} - (N_0 - N_{\text{Co}}) \mu_0 - N_H \mu_H \right], \quad (4.5)$$

where $G_{\text{slab}}^{\text{slab}}$ is the Gibbs free energy of the slab structure, $N_{\text{Co}}$, $N_0$, and $N_H$ refer to the number of Co, O, and H atoms, respectively, $g_{\text{CoO}}^{\text{bulk}}$ is the Gibbs free energy of bulk CoO, $A$ is the surface area of the supercell, and $\mu_H$ and $\mu_0$ are the chemical potentials of H and O, referenced to the gas phase H$_2$ and O$_2$ reservoirs, respectively. To interpret the surface free energy change respect to $\Delta \mu_O$, $\mu_O$ was translated using $\Delta \mu_O = \mu_O - \frac{1}{2} (E_{\text{O}_2(g)}^{\text{DFT}} + E_{\text{O}_2(g)}^{\text{ZPE}})$ at 0K and Equations 4.3 and 4.4. $\mu_H$ is defined as $\mu_H = \frac{1}{2} \mu_{\text{H}_2(g)} = \frac{1}{2} (E_{\text{H}_2(g)}^{\text{DFT}} + E_{\text{H}_2(g)}^{\text{ZPE}})$ at 0 K and used for the surface free energy calculation. The factor of two arises because two identical surfaces are included in the calculation in order to have a symmetric supercell. For surfaces with molecular adsorbates ($i$), the vibrational ($\Delta \text{ZPE}$) and entropic contributions (-$T \Delta S$) at 298 K of the adsorbates are included in the $G_{\text{slab}}^{\text{slab}}$ term in Equation 4.5 using $\Delta \text{ZPE} = \frac{1}{2} \sum_i \hbar \omega_i$ and $\Delta S = -k_B \sum_i \ln \left(1 - \exp \left(\frac{\hbar \omega_i}{k_B T}\right)\right)$.

Figure 4-3 shows the surface phase diagram (surface free energy as a function of $\Delta \mu_O$) for selected surface phases, including those found to be the most thermodynamically stable phase for some range of $\Delta \mu_O$; Figure 4-4 includes all of the other surface phases that were computed in order to determine the phase diagram. Examination of Figure 4-3 shows that under most conditions relevant to water splitting, phases with CoO(111) orientation are the most stable, with the exception of a narrow range (-0.466 $\leq \Delta \mu_O \leq$ -0.418, inset of Figure 4-3) in which clean CoO(100) is the most thermodynamically stable surface. Under oxygen-lean conditions ($\Delta \mu_O \leq$ -1.26), Co/CoO(111) is the most thermodynamically favorable surface, while the CoO(111) surface with a full monolayer of adsorbed H (denoted H*-CoO(111)) becomes favored...
with increasing oxygen partial pressure (-1.26 ≤ Δμ_Ο ≤ -0.466). Under oxygen rich conditions (Δμ_Ο ≥ -0.418), on the other hand, the fully hydroxylated-CoO(111) surface (denoted OH*-CoO(111)) is the most thermodynamically stable surface phase. This is in accordance with the experimental XPS demonstration of hydroxyl groups on the surfaces in CoO powder [88-89].

![Figure 4-3](image)

**Figure 4-3** Left: Surface Gibbs free energy of bare and H, O, OH adsorbed Co/CoO(111), CoO(100) and CoO(111) with respect to Δμ_Ο. The inset is the magnified view of the range -0.5 < Δμ_Ο < -0.4. Right: Surface configurations for the four phases found to be thermodynamically stable within the range -2.0 < Δμ_Ο < 0.5. Blue, red, and white circles denote Co, O, and H, respectively.
Figure 4.4 Plot of surface free energy of all surface configurations considered in this study versus $\Delta \mu_O$. OH*, O* and H* in the inset denote the species of adsorbate. The number (0.5 or 1) in parenthesis indicates the adsorbate coverage per surface unit cell. Co/ indicates a metallic Co layer on a CoO substrate. (100), (111) are the surface crystallographic orientations.

4.1.5 Morphology of CoO nanoparticles

The shape of nanoparticles can significantly impact their properties, not only because of different surface configurations, but also because of their different surface areas. The equilibrium shape of a crystalline substance is dominated by surfaces with relatively low surface energies, and can be constructed using the Wulff construction, which results in a polyhedron that relies only on ratios between surface energies and minimizes the total surface free energy of a fixed volume of a material [90]. We use the Wulffman program [91] to determine the Wulff construction of CoO nanocrystals under varying conditions. The results are illustrated in Figure 4-5. At $\Delta \mu_O = -0.60$, CoO particle has a truncated octahedron composed of clean CoO(100) and H*-CoO(111) surfaces. The area of clean CoO(100) reduces as $\Delta \mu_O$ becomes more negative, forming an octahedron shape that consists of only H*-CoO(111) facets under more oxygen-lean conditions ($-1.26 \leq \Delta \mu_O \leq -0.76$). Upon further decreasing the oxygen chemical potential ($\Delta \mu_O \leq -1.26$), the H desorbs from the H*-CoO(111) surface and a monolayer of oxygen vacancies form, resulting in an octahedron with only Co/CoO(111) facets.

As Figure 4-5 shows, starting from the truncated octahedron with clean CoO(100) and H*-CoO(111) facets at $\Delta \mu_O = -0.6$, increasing the oxygen chemical potential increases the relative surface area of the
clean CoO(100) facets. At $\Delta \mu _O = -0.44$, the morphology of the particle becomes almost cuboctahedron, while still retaining the CoO(100) and H*-CoO(111) facets, then the H*-CoO(111) facets subsequently change to OH*-CoO(111) to form a cuboctahedron-like shape. Further increasing $\Delta \mu _O$, the morphology of the nanocrystal evolves into a truncated octahedron by gradually decreasing the area of the CoO(100) facets while expanding the OH*-CoO(111) ones. Eventually, for $\Delta \mu _O \geq -0.12$, the nanocrystal becomes an octahedron consisting of only OH*-CoO(111) facets.

The oxygen partial pressure under which water splitting experiments are performed is about $P_{O_2} = 10^{-12}$ atm, which corresponds to $\Delta \mu _O = -0.355$. At this value of $\Delta \mu _O$, we predict CoO nanoparticles will have a truncated octahedron shape composed of CoO(100) and OH*-CoO(111) facets. More generally, we expect to observe roughly spherical nanoparticles over the range $-0.62 \leq \Delta \mu _O \leq -0.2$. Our predicted nanoparticle morphology is thus consistent with the experimental observations that CoO nanoparticles exhibit a spherical shape before and after water splitting [1].

![Figure 4-5](image)

**Figure 4-5** Optimal morphology of CoO nanocrystal estimated with Wulff construction at various $\Delta \mu _O$. The blue, green, yellow and red surfaces denote Co/CoO(111), H*-CoO(111), CoO(100), and OH*-CoO(111) surfaces, respectively.

### 4.1.6 $E_C$ and $E_V$ of CoO surfaces in vacuum

Figure 4-6 shows the computed conduction and valence band edge positions for CoO slabs with different surface configurations in vacuum. The band gap energy ($E_g$), conduction band edge energy ($E_C$), valence band edge energy ($E_V$), and work function ($\Phi$) of the thermodynamically stable surface
configurations are summarized in Table 4-1. We find that the band edge positions in Figure 4-6 do not match the experimental observations: The band edge positions of the OH*-CoO(111) and CoO(100) surfaces on CoO nanoparticles indicate that overall water splitting is infeasible since none of the CoO(100) and the OH*-CoO(111) surfaces does not have $E_V$ more positive relative to water oxidizing level ($H_2O/O_2$), differently from the experimental observation of overall water splitting in CoO nanoparticle suspension. However, the band edges of H*-CoO(111) on CoO micropowder span the water redox potentials, which is optimal for both $H_2$ and $O_2$ evolution, while experiments show that the conduction band edge of micro-sized particles is located far below the $H^*/H_2$ level, and thus overall water splitting cannot occur. Furthermore, although CoO(100) surface has the electronic structure very close to that of bulk CoO, in both the calculation (Figure 4-1) and the experimental measurements, the band edge positions of the CoO(100) surface is appropriate only for $H_2$ evolution, which is different from the flat band potential measurements of bulk CoO, in which bulk CoO has a conduction band edge located below $H^*/H_2$ level by 0.6 – 1.5 V.

![Figure 4-6](image)

**Figure 4-6** Conduction and valence band edge positions of CoO surfaces relative to the $H^*/H_2$ level, as predicted for slabs modeled in vacuum. Red (green) horizontal lines denote the conduction (valence) band edges of CoO surfaces. Dashed lines indicate water redox levels, $H^*/H_2$ and $H_2O/O_2$. The energy of the conduction band edge of each surface was determined by adding the experimental band gap (2.6 eV) from the energy of the computed valence band edge.

**Table 4-1** Band gap energies ($E_g$), energies of conduction band and valence band relative to vacuum level ($E_C$ and $E_V$), work function ($\Phi$) of bulk CoO, CoO(100), CoO(111), H*-CoO(111), OH*-CoO(111), Co/CoO(111) and Co(0001) slabs. CoO core in Co/CoO(111) means the central region of the whole symmetric Co/CoO(111) supercell, the structure of which was fixed to have the same lattice parameter as that of bulk CoO during structural relaxation of the slab.
<table>
<thead>
<tr>
<th></th>
<th>$E_g$</th>
<th>$E_C$</th>
<th>$E_V$</th>
<th>$\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk CoO (exp. [10]), pH = 0</td>
<td>2.6</td>
<td>5.2</td>
<td>7.8</td>
<td>-</td>
</tr>
<tr>
<td>Bulk CoO (exp. [10]), pH = 7.6</td>
<td>2.6</td>
<td>4.39</td>
<td>6.99</td>
<td>5.69</td>
</tr>
<tr>
<td>Bulk CoO</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CoO(100)</td>
<td>2.0</td>
<td>3.21</td>
<td>5.21</td>
<td>5.21</td>
</tr>
<tr>
<td>CoO(111)</td>
<td>2.5</td>
<td>3.78</td>
<td>6.27</td>
<td>4.69</td>
</tr>
<tr>
<td>H*-CoO(111)</td>
<td>2.7</td>
<td>3.28</td>
<td>5.95</td>
<td>5.74</td>
</tr>
<tr>
<td>OH*-CoO(111)</td>
<td>2.5</td>
<td>0.58</td>
<td>3.10</td>
<td>2.45</td>
</tr>
<tr>
<td>Co/CoO(111)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.00</td>
</tr>
<tr>
<td>CoO core in Co/CoO(111)</td>
<td>2.55</td>
<td>2.66</td>
<td>5.21</td>
<td>-</td>
</tr>
</tbody>
</table>

We tested the effect of employing an implicit solvation model using a polarization continuum model (PCM) via the VASPsol subroutine, which applies a relative permittivity value of 80 to mimic the water environment. We find that the band edge positions do not significantly change compared to those predicted in vacuum without the PCM. This suggests that explicit water is necessary to accurately compute the band edge positions of CoO slabs in water.

### 4.1.7 $E_C$ and $E_V$ of CoO surfaces in water

To predict the surface-dependent band edge position of CoO, we consider CoO/water interfaces with direct contact between the CoO surface and explicit water molecules, as various methods used in previous studies, including the absolute vacuum reference method [92] and Polarizable Continuum Models (PCMs) [93-94], have been unable to explain the band edge positions of CoO nanoparticles that have been experimentally observed using flat-band potential measurements (Figure 4-6).

To investigate the position of the $E_C$ of CoO surfaces relative to the water reduction potential (H$^+$/H$_2$ potential) level, we use an approach introduced in Ref. 60. In this approach (Figure 3-4), we first find the energy difference between the conduction band edge and the average Hartree potential of bulk CoO ($E_C^{\text{CoO(bulk)}} - H^{\text{CoO(bulk)}}$). Next, we compute the energy difference between the H$^+$/H$_2$ level and the average Hartree potential of bulk water ($\Delta^{\text{water(bulk)}} - H^{\text{water(bulk)}}$). Finally, we determine the difference between the Hartree potential in the CoO slab and in the central region of the water molecules for the CoO slab/water interface ($H^{\text{CoO(interface)}} - H^{\text{water(interface)}}$). We note that, unlike previous work developed for the prediction of the conduction band edge position of several bulk materials with respect to $E$(H$^+$/H$_2$), in which the material/water interface is constructed from an ideally cleaved bulk surface, we perform the third step using the DFT-optimized CoO surfaces in order to predict the surface-dependent band edge
position relative to H\textsuperscript{+}/H\textsubscript{2} level. For 1\textsuperscript{st} steps (bulk CoO) in this study, we find $E_{\text{C}}^{\text{CoO(bulk)}} - H^{\text{CoO(bulk)}} = 5.12$ eV.

### 4.1.7.1 H\textsuperscript{+}/H\textsubscript{2} level of bulk liquid water

The H\textsuperscript{+}/H\textsubscript{2} acceptor level in bulk liquid water is determined using the approach described in Ref. 60. Figures 4-8(a) and (b) show the atomic configurations of bulk liquid water and hydronium ion (H\textsubscript{3}O\textsuperscript{+})-containing liquid water (H\textsubscript{3}O\textsuperscript{+}/water). The electronic DOSs are obtained for the initial structures of pure bulk liquid water (Figure 4-7(a)) and the H\textsubscript{3}O\textsuperscript{+}/water system (Figure 4-7(b)) and shown in Figures 4-8(c) and (d). The local DOS of H\textsubscript{3}O\textsuperscript{+} in the H\textsubscript{3}O\textsuperscript{+}/water system was extracted and superimposed on the total DOS of the H\textsubscript{3}O\textsuperscript{+}/liquid water system (Figure 4-7(d)). As the figure shows, an additional peak around 1.2 eV is observed in the pure water band gap region ($E-E_F = 0 - 3$ eV) when H\textsubscript{3}O\textsuperscript{+} is added to the system. Based on this peak position (i.e., the LUMO of the H\textsubscript{3}O\textsuperscript{+}/water system), we find $A_{\text{water(bulk)}} - H_{\text{water(bulk)}} = -2.40$ eV for 2\textsuperscript{nd} step in the three step approach.
**Figure 4-7** Atomic configurations of (a) pure liquid water and (b) liquid water with H$_3$O$^+$ (1 H$_2$O$^+$ in 140 H$_2$O). Total DOS of (c) pure liquid water and (d) a H$_3$O$^+$-including liquid water system with respect to the valence band edge, $E_v$. The black line is the total DOS of H$_3$O$^+/water, the red the local DOS (LDOS) of the H$_3$O$^+$ ion in the system in Figure (b). The LDOS of the H$_3$O$^+$ ion is scaled by a factor of 15 to make it clearly visible on the scale of the total DOS.

4.1.7.2 Loss of magnetic moments of Co atoms in water

Experimentally, it has been observed that the Co atoms in the surface layer of CoO nanoparticles lose their bulk magnetic ordering in water. Our calculation on the interface of CoO slab/water also shows that CoO slabs in water exhibit electronic structure similar to that of non-magnetic CoO slabs in vacuum and in water (Figure 4-8(a) and (b)). To examine how much Co atoms existing in the surface layer lose their magnetic moments in direct contact with water molecules, the magnetic moments of the Co atoms were investigated, as shown in Figure 4-9. For comparison, the magnetic moments of the Co atoms in the CoO slab in vacuum are also shown. In comparison with the magnetic moments of Co atoms in vacuum (metallic Co layer in the Co/CoO(111) slab has $\sim 2 \mu_B$, the other CoO slabs have 2.7~2.8 $\mu_B$), the magnetic moments are considerably reduced in water (metallic Co layer in the Co/CoO(111) slab has $\sim 0.25 \mu_B$, the other CoO slabs have 0.6 $\mu_B$) regardless of surface configurations. This suggests that the interaction with water molecules suppresses the CoO magnetization, in agreement with the experimental observations [95].
Figure 4-8 Projected density of states (pDOS) of surface layer of CoO(100) slab versus $E-E_F$ computed (a) without spin polarization in vacuum; (b) without spin polarization in contact with explicit water; (c) with spin polarization in contact of explicit water; (d) with spin polarization in vacuum; (e) Bulk CoO for reference. Black, orange, blue, pink, green, solid lines denote the pDOS of O $s$, O $p$, Co $s$, Co $p$ and Co $d$ orbitals, respectively.
The loss of magnetic moments per Co atom due to the interaction with water molecules is closely related to the modification of spin density distribution in a Co atom as shown in Figure 4-10. Figure 4-10 shows the distributions of effective spin density obtained with a difference of the numbers of valence electrons with up and down spin states, \( N^\uparrow - N^\downarrow \), in AFM-II CoO(100) slab in vacuum and in contact with explicit liquid water. In vacuum (a to c in Figure 4-10), CoO(100) slab has up (yellow shade) or down (sky blue shade) spin along alternating (111) planes of Co atoms as we expected. However, CoO(100) slab in contact with liquid water (d to f in Figure 4-10) shows a mixture of electrons in up and down spin states in a Co atom nearby water molecules. This disordered spin state makes it hard to discern whether each Co atom is in either up or down spin state, which is responsible for the loss of magnetic moments per Co atom as shown in Figure 4-9. Thus, the long-range order of AFM-II configurations in CoO(100) slab in vacuum disappears after contact of water.
The changes in the spin density distribution (Figure 4-10) and magnetic moments of Co atoms (Figure 4-9) stem from the variation in the occupation of up and down-spin energy states in Co atoms induced by water contact. Figure 4-11 shows the orbital projected DOS (pDOS) of a Co atom in a surface layer of AFM-II CoO(100) slab in vacuum (Figure 4-11(a) and in contact with explicit liquid water (Figure 4-11(b)). Before water contact, $d$ orbitals of a Co atom in CoO(100) slab are filled with different numbers of electrons in up and down spin states, showing spin asymmetry, as observed in bulk phase (Figure 4-11(c) and (d)). This spin asymmetry is the origin of the magnetic moment of 2.6 $\mu_B$ from the contribution of Co $d$ orbitals, $N \uparrow - N \downarrow = 2.6$. However, water molecules in contact with the slab (Figure 4-11(b)) weakens the spin orbit coupling, which in turn enables the similar number of up and down spin electrons to fill the energy states below Fermi level. Therefore, the net atomic magnetic moments of the Co atom contributed from the $d$ orbital is $\sim 0.07 \mu_B$, which suggests that water contact causes magnetic to non-magnetic phase transition in the CoO slab. Additionally, it is observed that the total number of electrons, $N \uparrow + N \downarrow$, in $d$ orbitals increases after a contact with water (from 7.07 in bulk phase to 8.01 in contact with water). This increase must come from electron transfer from water to CoO slab to reach the electrochemical potential equilibrium. This also agrees with the band bending direction in CoO slabs explained in Figure 4-16.

![Projected DOS (pDOS) of a Co atom in a surface layer of AFM-II CoO(100) slab](image)

**Figure 4-11** Projected DOS (pDOS) of a Co atom in a surface layer of AFM-II CoO(100) slab (a) in vacuum and (b) in contact with explicit liquid water. Spin up and spin down pDOS are represented with positive and negative values, respectively. DOSs of Co $s$ and $p$ orbitals are very low compared to those of Co $d$ orbitals (blue and navy in figures). pDOSs of a Co atom in bulk phase (c) with down spin state and (d) with up spin state are shown as examples for reference. Figures on the right side of (b) and (d) present the integrated DOSs (blue is valence electrons with up spin ($N \uparrow$) blue and pink is valence electrons with down spin) ($N \downarrow$).
4.1.7.3 Change in $U_{\text{eff}}$ of Co atoms in water

CoO is a well-known Mott-Hubbard insulator in which on-site Coulomb interaction ($U$) splits the $d$-band into lower and upper Hubbard bands. As can be seen in Figures 3-2 and 4-2, bulk CoO and CoO(100) slab in vacuum show typical $d$-band aspects of a Mott-Hubbard insulator. However, as demonstrated in Figures 4-9, 4-10, 4-11 and 4-12, CoO(100) slab loses long-range antiferromagnetic nature in an aqueous environment because of the significant reduction in magnetic moments of Co atoms, eventually causing the disappearance of Hubbard $d$-bands splitting.

This change in $d$-bands in water contact can also be affected by the delocalization of electrons in $d$-bands caused by weakened Coulomb repulsion; single $d$-band appears with negligible on-site Coulomb repulsion ($U$) compared to hopping integral ($t$) needed for electron hopping between nearest neighbor sites, $t/U \ll 1$ [96-97]. To investigate whether on-site Coulomb repulsion remains in the CoO slab even after the contact with water, we compare the projected density of states (pDOS) of Co $d$ orbitals in a surface layer of CoO(100) slab in vacuum and in contact with explicit water, with variation of $U_{\text{eff}}$ as shown in Figure 4-12(a). The application of $U_{\text{eff}}$ to the slab/water interface is unable to induce the $d$-band splitting, albeit the $d$-band splitting occurs in bulk phase under the same conditions (Figure 4-12(b)). It is evident that $d$-band delocalization occurs in the CoO/water interface regardless of the $U_{\text{eff}}$ values. Consequently, we do not consider $U_{\text{eff}}$ for the calculation of the potential drop at the CoO/water for the prediction of the band edge position with explicit solvation method. The conduction band edge positions calculated with non-magnetic phase without $U_{\text{eff}}$ value in contact with water agree well with the experimental values in magnetic material systems including CoO, NiO and FeO as we described in Section 4.3, even though their ground states are AFM and the AFM is well described with appropriate $U_{\text{eff}}$ value in vacuum and in bulk phase (Section 4.3).
Figure 4-12 (a) Projected density of states (pDOS) of Co \( d \) orbital in a surface layer of CoO(100) slab with respect to \( E-E_F \) computed with various \( U_{\text{eff}} \) in vacuum (green line) and in contact with explicit water (orange line). (b) pDOS of Co \( d \) orbitals in bulk CoO with respect to \( E-E_F \) computed with various \( U_{\text{eff}} \) for reference. Due to the loss of magnetic moments of Co atoms in CoO slabs after contact with explicit water (Figures 4-10, 4-11, 4-12), spin polarization is not considered.

4.1.7.4 \( E_C \) vs. \( H^+/H_2 \) in an aqueous environment

To determine \( (H^{\text{CoO(interface)}} - H^{\text{water(interface)}}) \), the separately relaxed CoO slabs and water molecules are positioned in contact with each other as shown in Figure 4-13(a) as an example. The calculated planar averaged Hartree potential of the CoO/water layer of this example is plotted as a function of position in Figure 4-13(b). The computed potential differences at the interface for the Co/CoO(111)/water, H-CoO(111)/water, CoO(100)/water, and OH*-CoO(111)/water interfaces are summarized in Table 4-2. The corresponding conduction band edge energies (\( E_C \)) relative to the \( E(H^+/H_2) \) level of water are also evaluated for each interface. The calculated values, also reported in Table 4-2, are referenced to the normal hydrogen electrode, \( V_{\text{NHE}} \), using the relationship \( E_C^{\text{edge}} - E(H^+/H_2) = -e \times V_{\text{NHE}} \).
Figure 4-13 (a) Snapshot of the atomic distribution of the CoO(100)/water interface. Blue, red, and green circles indicate Co, O, and H atoms, respectively. (b) Planar-averaged Hartree potential of the CoO(100)/water interface computed for the structure shown in (a). Dotted line in (b) indicates macro-averaged Hartree potentials obtained using the approach in Ref. 98.

Table 4-2 The values in three step calculations and final conduction band energy ($E_C$) relative to $E(H^+/H_2)$ level of water at pH=1. The band edge position of the bare CoO(111)/water interface is shown for comparison. The value of $E_C$ relative to $E(H^+/H_2)$ is calculated through $(E_C^{\text{CoO}(\text{bulk})} - H^{\text{CoO}(\text{bulk})}) - (A^{\text{water}(\text{bulk})} - H^{\text{water}(\text{bulk})}) + (H^{\text{CoO}(\text{interface})} - H^{\text{water}(\text{interface})})$ [60]. Units are in eV.

<table>
<thead>
<tr>
<th>Bulk CoO</th>
<th>Bulk water</th>
<th>Interface of CoO/water</th>
</tr>
</thead>
<tbody>
<tr>
<td>£5.12</td>
<td>-2.40</td>
<td></td>
</tr>
<tr>
<td>Bulk CoO</td>
<td>-8.45</td>
<td>-0.93</td>
</tr>
<tr>
<td>Co/CoO(111)</td>
<td>-6.90</td>
<td>0.62</td>
</tr>
<tr>
<td>CoO(100)</td>
<td>-9.16</td>
<td>-1.64</td>
</tr>
<tr>
<td>OH*-CoO(111)</td>
<td>-6.97</td>
<td>0.55</td>
</tr>
<tr>
<td>H*-CoO(111)</td>
<td>-8.58</td>
<td>-1.06</td>
</tr>
<tr>
<td>CoO(111)</td>
<td>-7.57</td>
<td>-0.05</td>
</tr>
</tbody>
</table>

Figure 4-14 shows the computed band edges of bulk CoO and the different CoO surfaces relative to the water redox levels. In order to compare directly to the experimental measurements [1], the band edge positions are shifted from pH = 1 to pH = 7 in the plot by using the -0.059 V/pH unit relationship [99]. As the figure shows, we find that the conduction band edge of bulk CoO is approximately 0.93 V below the $H^+/H_2$ potential level, consistent with experiments, which show that the conduction band edge of bulk CoO is 0.6 –1.5 V below the $H^+/H_2$ [1,10]. This observation confirms again that bulk CoO is not
photocatalytically active; it also explains, from the band edge position point of view, why CoO micropowder is unable to split water, as the relatively large particles present in a CoO micropowder have the characteristics of bulk CoO.

The conduction band edges of both the H*-CoO(111) and CoO(100) surfaces are significantly below the H*/H$_2$, and similar to the experimentally measured values for bulk CoO and CoO micropowder. For the case of the CoO(100) surface, the minimal change in band edge positions relative to bulk is due to the bulk-like atomic configuration of the surface, which is also charge balanced. In the H*-CoO(111) case, the band edges remain similar to those in bulk CoO because H passivates all of the dangling bonds on the surface yet does not lead to a strong surface dipole. The decreased charge density at the surface of the H*-CoO(111) compared to that at the CoO(111) in Figure 4-15(c) confirms that passivation has occurred on the bare CoO(111) due to hydrogen adsorption, which in turn shifts the band edges to more positive potential (vs. NHE) than bare CoO(111). We note that we find these two surfaces to be thermodynamically favorable in the middle range of $\Delta \mu_O$ relevant to water splitting (Figure 4-5). As CoO micropowder is prepared under mildly reducing conditions ($\Delta \mu_O \sim -0.53$) [1], we hypothesize that only H*-CoO(111) and/or CoO(100) surfaces are present in the micropowder, thus explaining the lack of photocatalytic activity. Experimental confirmation of the existing surface facets in CoO micropowder is needed to confirm this hypothesis.

In contrast to the H*-CoO(111) and CoO(100) surfaces, the conduction band edge of the OH*-CoO(111) surface, which is predicted to be thermodynamically stable under the conditions for which overall water splitting has been observed, is located above the H*/H$_2$ level, while the valence band edge is below the H$_2$O/O$_2$ level. This shift in the band edges relative to bulk CoO arises from a surface dipole induced by the hydroxyl adsorption, as evidenced by the significant increase in the surface charge density in the OH*-CoO(111) compared to that of bare CoO(111), shown in Figures 4-16(f) and 4-16(d). Thus, we expect that particles with OH*-CoO(111) surfaces can induce both water oxidation and reduction. Very recent experimental results has proven the overall water splitting on the OH*-CoO(111) surfaces on sub-micrometer CoO octahedrons [57], even though the octahedral micropowders consisting of only OH*-CoO(111) facets showed a much lower photocatalytic efficiency compared to the CoO nanoparticles in Ref. 1. We discussed in Section 4.2 about why CoO nanoparticles exhibited a higher catalysis efficiency than the octahedral CoO micropowder. Consequently, the experimentally observed overall water splitting on CoO nanocrystals has been correlated with the presence of OH*-CoO(111) facets [1].

Surprisingly, the band gap of Co/CoO(111) surfaces, which we predict to exist in the most oxygen-lean conditions, also spans both the water reduction and oxidation potentials. This is also a result of surface dipoles related to the formation of the metallic Co layer (Figure 4-15(e)), similar to the origin of the band
edge shift of OH*-CoO(111) case. The band edge position of the Co/CoO(111) suggests the theoretical possibility of overall water splitting with the existence of a metallic Co layer on the (111) surface of CoO particles. This may explain the improved hydrogen-evolving catalytic performance recently observed for CoO(111)/Co core shell nanowires [89].

**Figure 4-14** Left: Band edge positions of CoO micro- and nano-particles estimated from flat band potential at pH=7 [1]. Right: Band edge position of the predicted thermodynamically stable surfaces of CoO relative to the water redox levels at pH=7. Red (green) horizontal lines denote the conduction (valence) band edges of each surface. Dashed lines indicate the water reduction (H+/H2) and oxidation (H2O/O2) potentials. The valence band edge of each surface is determined by subtracting 2.6 eV (the experimentally measured CoO band gap [1,10,78,100,101]) from the computed conduction band edge positions, EV (vs. H+/H2) = EC (vs. H+/H2) – E_{gap}^{expt}, since the major charge carriers between CoO surfaces and polar water are electrons, as discussed in Section 4.3.
Figure 4-15 (a) Average total charge density ($\rho$) of each layer in CoO(111) slabs along the direction parallel to the thickness ($z$-axis). Charge density difference ($\Delta \rho$) of (b) CoO(100), (c) $H^*$-CoO(111), (d) CoO(111), (e) Co/CoO(111), and (f) $OH^*$-CoO(111) slabs. Surface charges in (b)-(f) are referenced to the average charge of the bare CoO(111) surface shown in (a), i.e., $\Delta \rho = \rho(z) - \bar{\rho}$ (bare CoO(111)).

As can be seen in Figure 4-15, the trend in charge density deviation relative to the bare CoO(111) correlates with the order of the relative band edge position shifts, as expected to be closely related to the semiconducting nature of the surface. From Figure 4-15(b) to Figure 4-15(f), the deviation from the reference value at the surface layer increases monotonically from negative to positive. This implies CoO(100) is more positively charged, while $OH^*$-CoO(111) is more negatively charged, suggesting that the more $p$-type semiconducting nature of the surface leads to the more positive band edge position vs. NHE. Thus, we conclude that the significant upshift of the band edge position with reduction in particle size observed in CoO arises from the more $n$-type semiconducting nature of the $OH^*$-CoO(111).
4.1.8 Band bending at CoO surfaces in water

Recently, Greiner et al. [102] suggested that the energy band alignment of an oxide material is determined mainly by the equilibration of its electrochemical-potential \textit{i.e.}, Fermi levels, with the oxidation/reduction potentials of adsorbed molecules, despite the variation in the electronic properties with material. This makes sense because the equilibration of the electrochemical potential is achieved by the process of electron transfer at the semiconductor and the electrolyte. The transfer of electrons across the interface generates a space charge layer in the semiconductor. As a result, the energies of the conduction /valence band edges are shifted relative to their bulk values at the interface.

Figure 4-16 shows the schematics of the conduction and valence band edge positions of CoO/water interfaces relative to those of the bulk CoO phase, which in turn shows the amount of band bending at each surface/water interface for the case of a thick slab or micropowder. In common, the energy band edges bend downwards at the interface, similar to the band bending in a typical \textit{p}-type semiconductor. This is also in accordance with the negative slope observed in the experimental Mott–Schottky plots of CoO [1,10,11,24], indicating the \textit{p}-type semiconducting nature of the prepared CoO micro- and nanoparticles. The amount of band bending is dependent on the surface configurations, similar to the concept that flat band potential is a property of the interface of a material/electrolyte [17]. As the band edges of a surface decreases in energy relative to the bulk, such as for CoO(100) and H*-CoO(111), the degree of band bending increases, while it decreases when the edges are at higher energy, as in the case of OH*-CoO(111) and Co/CoO(111). This means that more electrons transfer from water molecules to more \textit{p}-type semiconducting CoO(100) and H*-CoO(111) slabs than to less \textit{p}-type semiconducting OH*-CoO(111) and Co/CoO(111) slabs in the process of the electrochemical potential equilibrium of the slabs and water. This interpretation is also supported by the computed work functions of the surfaces, \textit{e.g.}, H*-CoO(111) (5.74 eV) and CoO(100) (5.2 eV) accept more electrons due to higher work functions, while Co/CoO(111) (4 eV) and OH*-CoO(111) (2.45 eV) are likely to accept less electron (Table 4-1).

Thus, it is clear that the different characteristics of CoO surfaces are affected by different surface chemistry such as a metallic Co layer, or hydrogen and hydroxyl adsorbates, as well as by surface orientation. This in turn affects the amount of electron transfer between CoO and water, the band bending at the CoO/water interface, and band edge positions relative to water redox potentials, all of which affect the photocatalytic capability for overall water splitting.
Figure 4-16 Schematics of the conduction and valence band edge positions of CoO/water interface relative to those of bulk CoO phase. The conduction and valence band edges of bulk CoO are determined by the experimentally observed values of fermi level of ~ 0.3 eV above the valence band edge [103-104] and $E_g = 2.6$ eV [1,10,78,100,101]. The horizontal gray dashed lines denote water reduction and oxidation levels ($H^+/H_2$ and $H_2O/O_2$), the solid gray lines are Fermi level ($E_F$) of the equilibrated CoO and water. The width of the space charge layer in the CoO was arbitrarily determined.

4.1.9 Summary

Using DFT calculations, we have investigated the role of surface orientation and composition on the band edge positions of CoO surfaces in contact with liquid water. We showed that four distinct CoO surface configurations are thermodynamically stable over a range of oxygen partial pressures, with a fully hydroxylated CoO(111) (OH*-CoO(111)) surface being the most favorable under conditions relevant to room-temperature photocatalytic water splitting. Based on the computed surface free energies, we predict that, under these conditions, CoO nanoparticles form as truncated octahedra with both CoO(100) and OH*-CoO(111) facets. We show that the presence of OH*-CoO(111) facets is responsible for the experimentally observed upward shift of the band edge positions of CoO nanoparticles relative to bulk CoO, which are optimal for overall photocatalytic water splitting. We also showed that including explicit water molecules in DFT calculations is essential for accurately modeling the surface band edge positions in an aqueous environment, e.g., flat band potential measurement, for the first time, enabling the prediction of the band edge positions of an antiferromagnetic material in direct contact with liquid water that are in good agreement with the experimental measurements. Our work emphasizes the importance of understanding the details of the oxide/water interface for understanding and predicting optoelectronic and catalytic properties of oxides in real aqueous environments.
4.2 Photocatalytic overall water splitting on CoO nanoparticles: Mechanism for spontaneous H₂ and O₂ evolutions under irradiation

4.2.1 Motivation and objectives

It has long been believed that optimal band edges relative to water redox potential of nanostructures is the origin of the stoichiometric H₂ and O₂ evolution, such that if conduction and valence band edges of semiconducting photocatalysts straddle the water redox potential, overall water splitting can occur on nanoparticle photocatalysts. Therefore, in principle, a semiconducting material with band gap greater than 1.23 eV which is the minimum potential required for H₂ and O₂ evolutions on an ideal photocatalyst at 298 K [105-106], dissociates water into stoichiometric H₂ and O₂ with the photogenerated electrons and holes. However, many experimental results have reported that band gap of semiconducting photocatalysts should be greater than 1.23 eV by ~ 0.3 — 0.5 eV to overcome kinetic barriers of both HER and OER [107-108].

However, the kinetic barriers of HER and OER vary on different surface states of various photocatalytic materials, thus, the optimal band gap for overall water splitting extends to roughly 1.9 — 2.3 eV. In addition, among the self-standing photocatalytic nanoparticles observed to promote overall water splitting [1,30-38], Cu₂O [31] does not have the required band alignment with the water redox levels. On the other hand, numerous cases have been observed in which only one reaction occurs (only HER or OER), even though the band edge positions of the catalyst material do satisfy the criteria for overall water splitting. These catalysts include CdS [109-113], MoS₂ [114-116], TiO₂ [117-118], SrTiO₃ [119-120], CdSe [4,7], ZnO [121-122], Nb₂O₅ [33], SiC [123], and Sn₂TiO₄ [124]. This provides insight that whether conduction (valence) band edge is negative (positive) than water reduction potential (H⁺/H₂) (oxidation potential (H₂O/O₂)) is not the criterion governing the feasibility of the HER (OER).

Our density functional theory (DFT) study of the CoO/water interface in section 4.1 suggested that the significant shift of the band edge position in CoO nanoparticles in an aqueous solution compared to those of CoO micropowder, stems from the presence of fully hydroxylated CoO(111) facets (OH*-CoO(111)). Despite the experimental flat band potential measurement [110] and the thermodynamic calculations (Section 4.1) that well explain the feasibility of the overall water splitting on CoO nanoparticles, a clear picture of how water is actually dissociated on these nanoparticles is still missing.

In section 4.2, we extend our previous work on the facet-dependent band edge positions of CoO in an aqueous environment, using first-principles calculations to elucidate the mechanism for charge separation in CoO nanoparticles and determine the feasibility of spontaneous overall photocatalytic water splitting by computing the HER and OER overpotentials on the relevant CoO facets under the electron/hole potentials induced by photon absorption. By determining the built-in potential between the two facets based
on their relative band edges and computing the relative charge accumulation on each, we show that electrons are driven to the CoO(100) facets and holes to the hydroxylated CoO(111) facets (OH*-CoO(111)). Using DFT calculations, we compute the energy barriers for each step along the OER and HER pathways on the two different facets, and compare the computed transition state energies to the energies of the photogenerated charge carriers in order to determine the feasibility of photocatalytically induced overall water splitting on these nanoparticles. Applying the new criteria that HER (OER) can occur if and only if the photo-induced electrons (holes) have sufficient energy to overcome the largest reaction barriers along the HER (OER) pathway, we predict that H₂ evolution preferentially occurs on the CoO(100) facets, while O₂ evolution occurs on the OH*-CoO(111) facets, enabling stoichiometric generation of H₂ and O₂ from H₂O on CoO nanoparticles with no overpotential or co-catalyst, even though the band edge positions do not satisfy the conventional criterion for overall water splitting. This mechanism also provides a general framework for understanding previously unexplained experimental observations of overall photocatalytic water splitting on other self-standing photocatalysts that are not predicted to have the required band alignment with respect to the water redox potentials, as well as new criteria for identifying and designing novel photocatalysts.

4.2.2 Charge separation in CoO nanoparticles

In a previous study in Section 4.1, we demonstrated the thermodynamic feasibility of overall water splitting on CoO nanocrystals by elucidating the surface-dependent band edge positions relative to the water redox potentials (step (i)). We showed that the thermodynamically preferred morphology of CoO nanoparticles in an aqueous environment is a truncated octahedron consisting of two facets: fully hydroxylated CoO(111) facets (denoted by OH*-CoO(111)) and bare CoO(100) facets. These two kinds of facets have very different band edge positions relative to the water redox potentials. In particular, the band edge positions of OH*-CoO(111) are shifted significantly upwards compared to CoO(100). As a result, the conduction band edge is located at a more negative potential than the water reduction potential level (H⁺/H₂), and the valence band edge is more positive than the water oxidation potential level (H₂O/O₂), thereby allowing for the possibility of overall water splitting. Once CoO nanoparticles in water are exposed to light, the OH*-CoO(111) surface absorbs light of energy greater than 2.6 eV, and generates electron-hole pairs that have sufficiently high energy for both the hydrogen and oxygen evolution reactions (HER and OER) to occur. However, how both reactions take place on the facets of CoO nanoparticles has not yet been understood. Therefore, in this study we investigate the separation process of the photogenerated charge carriers (step (ii)) and the HER and OER activities of the two facets (step (iii)).
Charge separation can occur when there is a driving force for photogenerated electrons and holes to move in different directions or spaces. This implies that charge separation can occur if facets with different charge affinity exist in the nanocrystal. As determined in our previous study in Section 4.1, the two kinds of facets predicted to be present in CoO nanoparticles in water have very different surface properties: the CoO(100) surface is likely to be positively charged, while the OH*-CoO(111) surface is negatively charged. Thus, photogenerated electrons are expected to move to the CoO(100) surfaces, whereas holes migrate to the OH*-CoO(111) surfaces. In addition to the charge density difference, the conduction and valence band edge diagram of a CoO nanocrystal in an aqueous environment (Figure 4-17), suggests that charges will be rapidly separated between the two facets due to the large potential difference (~ 2.19 V) between them, which creates a large electric field throughout the entire nanocrystal due to its small dimensions relative to the typical length scale of band bending in CoO. This electric field drives the photogenerated electrons towards the CoO(100) facets and holes towards the OH*-CoO(111) facets.

![Conduction and valence band edge diagram](image)

**Figure 4-17** Conduction and valence band edge diagram with respect to arbitrary position from CoO(100) to OH*-CoO(111) in contact with water. The bands are plotted with respect to NHE. The conduction and valence bands (blue lines) linking two facets are considered to be linear because they are unlikely to have the bulk-like structure in the central region, considering that the CoO nanocrystals used for the overall water splitting is ~ 10 nm in diameter, which is smaller than the general width of space charge layer (~ 10 nm ─ several µm [18]).

It is unclear, however, whether the charge separation still occurs when the two facets exist in conjunction with each other, since the charge density distributions studied in the previous work in Section 4.1 were obtained for isolated supercells. To confirm whether the charge separation indeed occurs in
realistic CoO nanocrystals, we consider a nanorod composed of CoO(100) and OH*-CoO(111) facets, as illustrated in Figure 4-18. In the supercell, we investigate how much the charge density of the surface in the nanorod deviates from the average value of CoO(111), as described in the methods section. The results are summarized in Table 4-3. We find that excess electrons are collected on the OH*-CoO(111) surface of the nanorod, as observed for the isolated slab with OH*-CoO(111) surfaces (Section 4.1). We also find a decrease in the electron charge density on the Co atoms in the outmost layer of the CoO(100) surface of the nanorod, similar to that observed for the isolated CoO(100) slab. This confirms our expectation that the charges will be separated between the two facets in actual CoO nanoparticles.

![Figure 4-18](image)

**Figure 4-18** (a) Atomic configuration of a CoO supercell constructed with OH*-CoO(111)(yellow shade) and CoO(100) (green shade) facets. (b) Side view of the prepared supercell. (c) Atomic configuration of a CoO nanorod that is constructed when the periodicity is applied to the prepared supercell along x-axis.

<table>
<thead>
<tr>
<th>Facet</th>
<th>Element in the outmost layer</th>
<th>( \Delta \rho )</th>
<th>( \Delta \rho ) in isolated slab</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH*-CoO(111)</td>
<td>O</td>
<td>0.124</td>
<td>0.114</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.210</td>
<td>0.207</td>
</tr>
<tr>
<td>CoO(100)</td>
<td>Co</td>
<td>-0.023</td>
<td>-0.043</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-0.019</td>
<td>-0.017</td>
</tr>
</tbody>
</table>

**Table 4-3** Deviation of charge density relative to average charge density of CoO(111), \( \Delta \rho \), in OH*-CoO(111) and CoO(100) facets in the supercell shown in Figure 4-18. The charge density difference was investigated for every atom and their averaged values were summarized. The change density differences calculated in the isolated OH*-CoO(111) and CoO(100) slabs (\( \Delta \rho \) in isolated slab) were shown together for reference.
4.2.3 Theoretical HER and OER overpotentials

In order for the separated charge carriers to overcome the kinetic barriers for formation of reaction intermediates on the surface of the electrode and to induce the HER or OER, some amount of excess energy, i.e., overpotential ($\eta$), is required. The magnitude of the overpotential determines how easily the reaction can occur, i.e., the activity for HER or OER. The theoretical electrochemical overpotential for HER or OER is defined as the difference between the energy level of the transition state of the limiting step in the reaction relative to H+/H$_2$ or H$_2$O/O$_2$ [125]. Therefore, the relative HER (OER) activity of CoO(100) and OH*-CoO(111) surfaces can be roughly estimated by the $E_C$ ($E_V$) relative to H+/H$_2$ (H$_2$O/O$_2$), as marked in Figure 4-19.

From the band edge position point of view, both the HER and OER overpotentials are lower on the OH*-CoO(111) surface compared to on the CoO(100) surface, and neither reaction should occur on the CoO(100) surface. However, it is difficult to conceive of a mechanism in which both O$_2$ and H$_2$ are simultaneously generated on the same facet. In particular, the photoexcited electrons are expected to move to the CoO(100) facets, and would therefore not be available for HER on the OH*-CoO(111) facets. On the other hand, if the photoexcited carriers are not separated to different facets as predicted, then we would expect high recombination rates and little to no O$_2$ or H$_2$ evolution. This suggests that the band edge positions with respect to the water redox levels may not be the most important metric for predicting photocatalytic activity. Instead, we hypothesize that the key property that determines whether photocatalytic HER or OER can occur on a given surface is the difference between the potential of the photo-excited electron or hole and the energy level of the transition state of the relevant rate limiting HER or OER step. Below, we investigate this hypothesis by using DFT to compute the free energies of the reaction steps for HER and OER on both the CoO(100) and OH*-CoO(111).
**Figure 4-19** Band edge positions of bulk CoO and the CoO(100) and OH*-CoO(111) facets relative to the water reduction/oxidation potential levels (Section 4.1). The red horizontal single line denotes the conduction band edge, while the green double line indicates the valence band edge. The relative HER overpotential is shown with orange dashed line ($\eta_{\text{HER}}$), the relative OER overpotential with blue dashed line ($\eta_{\text{OER}}$).

### 4.2.4 HER and OER activities under equilibrium potential

To begin, we determine the relative HER activities of the CoO(100) and OH*-CoO(111) surfaces by determining the free energy change for H adsorption ($\Delta G_{\text{H}}$) [28,63-66]. The value of $\Delta G_{\text{H}}$, can be computed by modeling the possible intermediates formed during the hydrogen adsorption-reduction-desorption processes at the cathode. We use the convention that negative $\Delta G_{\text{H}}$ indicates strong binding of hydrogen atoms to the surface, which blocks potential active sites and retards hydrogen generation, while positive $\Delta G_{\text{H}}$ indicates weak bonding of hydrogen atoms to the surface, which fails to stabilize intermediates and prevents any reaction from taking place. Thus, the highest HER activity is given by $\Delta G_{\text{H}}$ close to 0, according to the Sabatier principle [67-68].

Figure 4-20(a) shows the calculated free energy change for H adsorption ($\Delta G_{\text{H}}$) on the bare CoO(100) surface and CoO(111) surfaces with a range of OH coverage at the equilibrium potential ($U = 0$ V). As the figure shows, $\Delta G_{\text{H}}$ is positive for the bare CoO(100) surface, but negative for all CoO(111) surfaces, independent of OH coverage. The figure also shows that the absolute value of $\Delta G_{\text{H}}$ increases with increasing OH coverage, indicating that desorption of hydrogen from the surface becomes increasingly difficult with increasing OH coverage, thus inhibiting HER under standard conditions. Interestingly, our results also show that the sign of $\Delta G_{\text{H}}$ is determined by whether the conduction band edge of the surface is at a positive or negative potential relative to the standard water reduction potential, $E(\text{H}^+/\text{H}_2)$. For example, we find $\Delta G_{\text{H}} > 0$ on CoO(100) surfaces, which have a conduction band edge below $\text{H}^+/\text{H}_2$ (i.e., at a positive potential relative to $\text{H}^+/\text{H}_2$), while $\Delta G_{\text{H}} < 0$ for OH*-CoO(111) surfaces, which have a conduction band edge above $\text{H}^+/\text{H}_2$ (i.e., at negative potential relative to $\text{H}^+/\text{H}_2$). This indicates that a surface with the conduction band edge at a more negative (positive) potential relative to $\text{H}^+/\text{H}_2$ will attract hydrogen to the surface more strongly (weakly). We also find that the HER overpotential is smaller on CoO(100) than on OH*-CoO(111), in contrast to the HER overpotentials estimated from the band edge positions. We will discuss the meaning of the difference between the theoretical overpotential and the overpotential calculated from the intermediate state in the following section.

Like HER, the OER overpotential of a material can be estimated based on the binding energies of the intermediates on the surface relative to H$_2$O and H$_2$ in the gas phase. The proposed OER mechanism
consists of four consecutive proton and electron transfer steps with the intermediates \( \text{OH}^*, \text{O}^*, \text{OOH}^* \) and \( \text{OO}^*(\text{O}_2) \) [69]. The largest difference in the free energy change of the intermediates along the reaction path, \( i.e., \max[\Delta \text{G}_{\text{OH}^*}, \Delta \text{G}_{\text{O}^*}, \Delta \text{G}_{\text{OOH}^*}] \) [29], is taken to be the theoretical OER overpotential. The details are explained in section 3.5 in Methods.

Figure 4-20(b) shows the free energy diagram of the calculated free energies of the intermediates along the overall OER pathway, \( \Delta \text{G}_{\text{OH}^*}, \Delta \text{G}_{\text{O}^*}, \Delta \text{G}_{\text{OOH}^*} \) of the bare CoO(100), bare CoO(111) and OH*(3/4)-CoO(111) at the equilibrium potential \( (U = 1.23 \text{ V}) \). The CoO(100) surface has positive values for all \( \Delta \text{G}_{\text{OH}^*}, \Delta \text{G}_{\text{O}^*}, \Delta \text{G}_{\text{OOH}^*} \), implying that none of these adsorbates bind easily to the CoO(100) surface. However, the bare CoO(111) and OH*(3/4)-CoO(111) stabilize both the \text{O}^* and \text{OH}^* adsorbates. Furthermore, they have OER overpotentials \( (2.17 \text{ V for CoO(111), 1.18 V for OH*(3/4)-CoO(111))} \) much lower than that of CoO(100) \( (3.67 \text{ V}) \). As a result, we expect that OER occurs on OH*-CoO(111) facet.

**Figure 4-20** (a) Free energy change for hydrogen adsorption \( \Delta \text{G}_{\text{H}^*} \) of bare CoO(100) and CoO(111) with various OH coverage along the HER reaction coordinate at the equilibrium potential \( (U = 0 \text{ V}) \). (b) Free energy change of CoO(100), CoO(111) and OH*(3/4)-CoO(111) along the OER reaction coordinate at the equilibrium potential \( (U = 1.23 \text{ V}) \). All calculations were carried out with 1/4 coverage of the relevant adsorbates. In the legend of (a), the number in parenthesis is the OH coverage on the surface, and the 1/2 at the right side of ‘CoO(111)’ denotes that the energy change is calculated with the 1/2 H coverage.

**4.2.5 HER and OER activities at the photo-induced potential**

HER and OER overpotentials estimated from the binding energies of the reaction intermediates have been shown to agree with experimental electrochemical measurements. It is obvious in the case of an electrochemical cell, because some amount of energy should be supplied to an electrochemical catalyst to
Induce the reaction. The energy greatly depends on the intermediate state, which is given by the electrode potential required for the initiation of the reaction.

In the same way, previous studies have employed the calculated overpotentials to interpret photocatalytic behavior, as the reactions are expected to occur via the same mechanism. However, to date, HER and OER overpotential calculations on photocatalytic materials have been unable to explain experimental observations of spontaneous overall water splitting under a light source for a variety of materials. Recently, Montoya et al [126], investigated the relationship between the optimal band edge positions of various materials for overall water splitting and the HER and OER activities estimated from the binding energies of the intermediates. Based on the results of this study, the authors suggested that a co-catalyst must be present in order to induce both OER and HER reactions on the materials, even though their band edge positions are optimized for overall water splitting. However, the band edge positions in this study were estimated from an empirical relationship parameterized by the band gap of the bulk materials and the electronegativity of its constituent atoms [127], and predictions from this relationship were found to exhibit relatively large errors (up to ~ 0.5 eV) [10], which are hypothesized to originate from the incomplete understanding of the surface state of the materials in an aqueous environment. Even if the calculated band edge positions are comparable to the experimental values, the HER and OER overpotentials for the materials in Ref. 126 are calculated only for the (100) surfaces, since (100) is generally known to be the most stable for perovskite compounds [128]. Therefore, it is still an open question whether the clean (100) surface is in fact the surface upon which the reactions occur, and there is insufficient evidence to conclude that none of the various photocatalytic materials studied could simultaneously fulfill the requirements for lower overpotentials for both HER and OER.

Nevertheless, several nanoparticle photocatalysts have demonstrated stoichiometric generation of H₂ and O₂ without co-catalysts or externally applied potential under a light source [1,30-38]. Among the self-standing photocatalytic nanoparticles for overall water splitting, Cu₂O [31] shows that the band edges do not have the required alignment with the water redox levels for overall water splitting, yet H₂ and O₂ are still simultaneously evolved. On the other hand, cases have been observed in which only one reaction occurs, even though the band edge positions satisfy the criteria for overall water splitting (CdS [109-113], MoS₂ [114-116], TiO₂ [117-118], SrTiO₃ [119-120], CdSe [4,7], ZnO [121-122], Nb₂O₅ [33], SiC [123], and Sn₂TiO₄ [124]). To resolve this conundrum, we propose new criteria for screening the feasibility of HER and/or OER on a specific surface, i.e., that the energy of the photoexcited electrons is greater than that of the transition state for HER, and the energy of the photoexcited holes is greater than that of the transition state for the rate-limiting step of OER. Unlike the electrochemical cell, in a semiconducting photocatalyst, the energy state of the photogenerated charge carriers is determined by the band edge positions, which is
critical for light absorption. Therefore, the energy state of the charge carriers provided by light absorption should be sufficient to overcome the kinetic barrier of the reaction, i.e., the free energy of the transition state relative to that of the initial state.

Figure 4-21(a) shows the conduction and valence band edges that determine the potential levels of electrons and holes generated by photon absorption at the interface of OH*-CoO(111) and water. On the OH*-CoO(111) surface, the photogenerated electrons are at a potential 0.55 eV more negative than the H+/H₂, while the photogenerated holes are at a potential 2.05 eV more positive than the water reduction potential. In other words, the electrons have 0.55 eV extra energy for HER, while the holes have 0.82 eV extra energy for OER relative to an ideal photocatalyst. To determine the feasibility of HER and/or OER under the potential given by the photon absorption and charge carrier generation, we evaluate the energy states of the HER and OER intermediates as well as the overpotentials, as shown in Figures 4-22(b) and (c).

From the calculated thermodynamic stability (Section 4.1) as well as experimental observations with XPS [88,89], the CoO(111) surface is expected to be hydroxylated after equilibration in water, although the exact OH coverage is not known experimentally. However, performing ab initio molecular dynamics calculations of CoO(111) and OH*-CoO(111) in water (Figure A-1 in the Appendix), we find that complex surface configurations can be formed during the actual water splitting, which in turn can significantly alter the HER and OER overpotentials as shown in Figure 4-21(c), as well as Figures A-2 and A-3 in the Appendix.

Figure 4-21(b) shows the free energy changes of the OER intermediates along the reaction pathway under \( U = 2.05 \text{ V} \), the potential of the photogenerated holes. Our results predict that the photogenerated holes are able to trigger OER on the CoO(111) with half a monolayer of OH (OH*(1/2)-CoO(111)) without a reaction barrier, as indicated by the downhill free energy change for each step along the reaction pathway (dark green line). The OH*(1/2)-CoO(111) surface is the only one of the configurations considered here that is able to induce OER without an additional applied potential. This means that the transition state of the OH*(1/2)-CoO(111) exists at a slightly negative potential relative to the valence band edge at the surface (2.05 V), and therefore the potential for holes obtained from light absorption is sufficient to drive spontaneous OER. On the other hand, the transition states on the other surface configurations with various OH and O and H coverage are at positive potentials relative to the valence band edge at the surfaces. On these surfaces, an additional potential (overpotential) corresponding to the energy difference between the transition state and the valence band edge, \( E(TS) - E_V \), is required to overcome the kinetic barrier for OER under the light-induced potential.
We also investigate the feasibility of HER on the OH*-CoO(111) via photogenerated electrons by considering $\eta_{\text{HER}}$ under $U = -0.55$ V (Figure 4-21(c)). Since the overpotential depends strongly on the coverage of different species at the surface [129], we consider a range of possible surface configurations. Under $U = -0.55$ V, the $\eta_{\text{HER}}$ values for all surface configurations are shifted by $+0.55$ eV from those obtained under the standard potential due to $\eta_{\text{HER}}(U) = \Delta G_{H^*}/e(U = 0V) - U$ [211]. Among the considered surface configurations, we find that $\eta_{\text{HER}}$ goes from negative to positive when going from the standard potential to the potential of the photogenerated electrons (-0.55 V) only for the OH*(1/4)-O(1/4)-CoO(111)(O) surface. This means that one hydrogen of the hydroxyl group on the OH*(1/2)-CoO(111) surface is readily desorbed from the surface under the potential of the photogenerated electrons (inset of Figure 4-21(c)), spontaneously creating H$_2$. The other surface configurations in the negative range slightly relieve the strong binding energy by 0.55 eV. Yet, they still need additional potential to reach $\eta_{\text{HER}} = \sim 0$ to trigger HER. On the other hand, the photo-applied potential for electrons makes the positive $\eta_{\text{HER}}$ more positive, which indicates that photo-absorption makes it more difficult to adsorb hydrogen. Finally, we find that the CoO(111) surface with 1/2 OH coverage energetically favors HER by desorbing hydrogen from the hydroxyl group. It is interesting to note that, in principle, this surface could therefore simultaneously oxidize and reduce water with photogenerated carriers without an external bias. This explanation clarifies the origin of the photocatalytic overall water splitting on sub-micronmeter CoO octahedra covered with OH*-CoO(111) facets, but with lower efficiency [57] (the reason for the lower efficiency compared to spherical CoO nanoparticles is explained in section 4.2.6). However, as noted above, we expect that the relative populations of photoexcited electrons and holes at this surface will favor OER.
Figure 4-21 (a) Band edge position of OH*-CoO(111) surface and potential levels of photogenerated electrons and holes with respect to the water reduction potential level. (b) Free energy change of OH, O and H adsorbed CoO(111) surfaces along the OER reaction coordinate under 2.05 V. (c) HER overpotential (\(\eta_{HER}\)) on CoO(111) surfaces with a range of OH, O and H coverage under 0 V and -0.55 V. The legend in Figure (b) and vertical axis in Figure (c) denote the initial surface configuration prior to the adsorption of the intermediate species. The number in parenthesis next to the '*' indicates coverage of the species. The (O) in vertical axis of Figure (c) indicates that H adsorption (or desorption) was conducted by binding on the O site, as illustrated in the inset, rather than adsorbing at the clean surface site.

Unlike CoO(111), bare CoO(100) is predicted to maintain an ideal surface (no adsorbates) in an aqueous environment. Therefore, we assume that CoO(100) has clean surface sites during HER and OER except for the adsorption of the intermediates. Figure 4-22(a) shows the conduction and valence band edges of the bare CoO(100) surface. From the band edge positions, it can be seen that the potential level of electron-hole pairs given by photon absorption at the CoO(100)/water interface is +1.64 V for electrons and +4.25 V for holes with respect to the water reduction potential level.

Figure 4-22(b) shows the free energy change along the OER reaction coordinate under \(U = 4.25\) V. Even though the CoO(100) is under a very large positive potential, additional energy of \(~0.65\) eV is required
to overcome the reaction barrier for the reaction step going from OH* to O*; therefore, the photo-potential is not sufficient to induce OER on this surface. On the other hand, the original large HER overpotential of CoO(100) under \( U = 0 \) V is significantly reduced by the photogenerated potential for electrons (1.64 V). As a result, HER overpotential becomes close to zero under \( U = 1.64 \) V, suggesting that the HER is energetically feasible on the CoO(100) surface without an additional applied potential.

This is an unexpected finding, since it is generally accepted that HER occurs only when the conduction band edge position of a material is more negative than the water reduction potential. However, our results show that whether the reaction occurs is determined by the relative energy of the photogenerated carriers and the actual transition state of the reaction, thereby explaining the experimentally observed overall water splitting on CuO [31] despite the non-optimal band alignment, as well as the lack of overall water splitting on Sn2TiO4 [124], CdS [109-113,130-131], SiC [123], Nb2O5 [33], CdSe [4,7], SrTiO3 [119-120,132], despite the predicted optimal band alignment.

**Figure 4-22** (a) Band edge position of bare CoO(100) and potential levels of photogenerated electrons and holes with respect to water reduction potential level (b) Free energy change of bare CoO(100) surface along OER reaction coordinate under \( U = 4.25 \) V (c) HER overpotential \( (\eta^{HER}) \) of bare CoO(100) under \( U = 0 \) V (black line) and 1.64 V (blue line). All energy calculations are done with the adsorption of the reaction intermediate of 1/4 surface sites concentration.
It is possible that the potential level of charge carriers given by light absorption deviates from that of OH*-CoO(111) due to different surface coverage, although the dominant surface configuration of the CoO(111) in a water environment is considered to be hydroxylated. Thus, to more accurately assess the feasibility of HER and/or OER on various surface configurations, we compute the conduction and valence band edges of all surfaces. The results are summarized in Table 4-4. Based on the calculated band edge energies and the HER and OER overpotentials, the feasibility of the reaction is determined such that HER occurs when $E_C$ is more negative than $\eta_{HER}$ and OER proceeds when $E_V$ is more positive than $\eta_{OER}$. This criterion indicates that the absorbed light can overcome the kinetic barrier of the reactions. In accordance with the evaluation in Figures 4-22 and 4-23, HER is energetically feasible on CoO(100) and OER on CoO(111) with a hydroxyl coverage of one half.

**Table 4-4** Calculated conduction and valence band edge position ($E_C$ and $E_V$), HER and OER overpotentials ($\eta_{HER}$ and $\eta_{OER}$) under $U = 0$ V, feasibility of the HER and OER (f(HER) and f(OER)) determined based on the comparison of the band edge and the overpotential. Feasible reaction is marked with ‘O’, unfeasible reaction with ‘X’.

<table>
<thead>
<tr>
<th>Initial surface configurations</th>
<th>$E_C$</th>
<th>$E_V$</th>
<th>$\eta_{HER}$</th>
<th>$\eta_{OER}$</th>
<th>f(HER)</th>
<th>f(OER)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO(100)</td>
<td>1.640</td>
<td>4.250</td>
<td>1.631</td>
<td>4.898</td>
<td>O</td>
<td>X</td>
</tr>
<tr>
<td>CoO(111)</td>
<td>0.048</td>
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<td>-1.406</td>
<td>3.400</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>CoO(111)-1/2</td>
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<td>2.648</td>
<td>-1.081</td>
<td>3.310</td>
<td>X</td>
<td>X</td>
</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>OH*(1/4)-CoO(111)</td>
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<td>1.915</td>
<td>-1.791</td>
<td>4.640</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>OH*(1/2)-CoO(111)</td>
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<td>1.992</td>
<td>-1.586</td>
<td>2.000</td>
<td>X</td>
<td>O</td>
</tr>
<tr>
<td>OH*(3/4)-CoO(111)</td>
<td>-0.706</td>
<td>1.894</td>
<td>-2.252</td>
<td>2.410</td>
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<td>X</td>
</tr>
<tr>
<td>O*(1/2)-CoO(111)</td>
<td>0.680</td>
<td>3.280</td>
<td>0.378</td>
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<td></td>
</tr>
<tr>
<td>O*(1/2)-CoO(111)-1/2</td>
<td>0.680</td>
<td>3.280</td>
<td>0.150</td>
<td>3.654</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>OH*(1/4)-O*(1/4)-CoO(111)</td>
<td>-0.303</td>
<td>2.297</td>
<td>-0.716</td>
<td>4.564</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>OH*(1/4)-O*(1/4)-CoO(111)(O)</td>
<td>-0.303</td>
<td>2.297</td>
<td>-0.381</td>
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<td></td>
</tr>
<tr>
<td>OH*(1/2)-O*(1/4)-CoO(111)</td>
<td>-0.646</td>
<td>1.954</td>
<td>-1.954</td>
<td>3.088</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>OH*(1/2)-O*(1/4)-CoO(111)(O)</td>
<td>-0.646</td>
<td>1.954</td>
<td>-1.214</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH*(3/4)-O*(1/4)-CoO(111)(O)</td>
<td>-0.600</td>
<td>2.000</td>
<td>-1.940</td>
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<td></td>
</tr>
<tr>
<td>OH*(1/2)-H*(1/4)-CoO(111)</td>
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<td>2.333</td>
<td>-1.121</td>
<td>3.688</td>
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<td>X</td>
</tr>
<tr>
<td>H*(1/4)-CoO(111)</td>
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<td>4.160</td>
<td>-0.756</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>H*(1/2)-CoO(111)-1/2</td>
<td>0.656</td>
<td>3.256</td>
<td>-0.797</td>
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</table>

- $\eta_{HER}$ is similar to the HER overpotential of the surface, HER might be possible given the errors inherent to DFT. However, we expect the actual reaction rate would be negligible due to the high back reaction probability in the confined space of the nanoparticle.

- The band edge position during the reaction (along the HER and OER pathways) changes very little (Figure A-4 in the Appendix); therefore, the feasibility of the reaction is expected to be essentially constant during the reaction.
4.2.6 Overall water splitting on CoO nanoparticles

As mentioned in section 4.2.2, we predict that in CoO nanoparticles in water, photogenerated carriers are separated by a built-in potential, with electrons driven to CoO(100) surface facets, and holes driven to OH*-CoO(111) surface facets due to the difference in band edge positions at these surfaces. On the OH*-CoO(111) surface (Figure 4-21), our results suggest that the photogenerated holes will serve OER on a half hydroxylated region, while photogenerated electrons could enable HER by desorbing hydrogen from a half hydroxylated region. However, we expect the population of photogenerated electrons on OH*-CoO(111) surface to be very low due to the built-in potential, which will quickly sweep electrons away from the OH*-CoO(111) facet to CoO(100). Even if HER can be realized on the half hydroxylated CoO(111) before the photogenerated electrons are separated to the CoO(100) surface, the fraction of the hydrogen formed on the former facet in total HER would be very small, taking into account a high probability of back reaction owing to the confined space of the CoO nanoparticles. On the CoO(100) surface, which strongly attracts photogenerated electrons, OER is unlikely to occur because of a significant energy barrier which cannot be overcome by the photogenerated holes, but HER can readily occur using both the transferred electrons and the photogenerated electrons on the surface. Thus, we expect OER to primarily occur on the OH*-CoO(111) facets and HER to occur on the CoO(100) facets in the CoO nanoparticles.

Overall photocatalytic water splitting on CoO nanoparticles is thought to take place without a co-catalyst or external bias because the nanoparticle functions as either a co-catalyst-integrated nanoparticle or a p-n junction photocatalyst in which CoO(100) is a p-type semiconductor and OH*-CoO(111) is a n-type semiconductor. In addition, the spontaneous charge separation taking place in the CoO nanoparticles can largely improve photocatalytic efficiency, which supports the experimentally measured high photocatalytic efficiency (5%) of CoO nanoparticles [1]. Even though the nanoparticle is made of a homogeneous material, the different surface configurations with different charge densities and electron affinities on the nanoparticle enable advanced heterogeneous functions. Unlike the spherical CoO nanoparticles of high efficiency, sub-micrometer CoO octahedra covered with OH*-CoO(111) facet cannot separate e-h pairs because there is only one type of facet. Thus, even though the OH*-CoO(111) facet can conduct photocatalytic overall water splitting, the efficiency will be significantly reduced compared to the spherical CoO nanoparticles, as observed experimentally [57]. This understanding of overall photocatalytic water splitting on CoO nanoparticles may also explain how various other single-material nanoparticles can perform as photocatalysts for overall water splitting without a co-catalyst or external potential. Furthermore, it emphasizes that understanding photocatalytic water splitting requires knowledge of three key properties:

1) The morphology of the nanoparticle and the thermodynamically stable surface configurations in an
aqueous environment; 2) the energy state of the photogenerated charge carriers from calculation of the band edge positions; and 3) the relative energy of the transition state of the reaction under the photo-induced potential.

4.2.7 Summary

This study first suggests how overall water splitting can occur on a self-standing CoO nanoparticle photocatalyst with high photocatalytic efficiency and without a co-catalyst or external bias. We demonstrated that photogenerated charge carriers are separated onto different facets of the nanoparticles due to a strong electric field which is formed between the two facets because of their very different surface properties; electrons are driven to CoO(100) facets and holes to OH*-CoO(111) facets. Furthermore, we showed that the electrons transferred to the CoO(100) facets can trigger HER, while the holes on the OH*-CoO(111) facets can induce OER under the photo-given potential on each facet without an external bias because the photogenerated carriers have energies sufficient to overcome the kinetic barriers of the HER and OER. Finally, we suggested that feasibility of each reaction should be assessed by comparing the relative potential levels of the photogenerated carriers and the transition state, $E_C \leq \eta^{HER}$ for HER and $E_V \geq \eta^{OER}$, which can be used as a criterion for predicting the half reaction as well as overall water splitting on various materials.
4.3 Explicit solvation prediction of band edges of transition metal oxide photocatalysts: Optimal methodology for dealing with localized d orbitals in aqueous environments

4.3.1 Comparison of band edge positions in vacuum and in water

Valence and conduction band alignment relative to water redox potential is a critical property of photocatalytic materials for water splitting, which primarily determines the feasibility of HER and/or OER from water splitting under illumination. HER (OER) is known to occur when the conduction (valence) band edge is more negative (positive) than the hydrogen evolution potential level, \( \text{H}^+ / \text{H}_2 \) (oxygen evolution potential level, \( \text{H}_2\text{O} / \text{O}_2 \)). In nanostructured photocatalysts, the different band edge positions of several facets on the nanostructured systems, can play a crucial role in promoting the separation of the photogenerated charge carriers, which results in the improvement of photocatalytic efficiency [133-139].

The band edge positions relative to water redox potential levels are significantly influenced by materials [22,140-142], crystal structures [143-145], surface characteristics [138, 146-150], and operating environment of a photocatalyst [151-154]. In the equilibrium process of the electrochemical potentials of the photocatalyst and the adjacent medium (or electrolyte), electrons transfer across the surface/medium interface. The amount and the direction of the electron transfer is determined by the relative electrochemical potentials of the photocatalyst and the medium, which are largely affected by the different surface environments. As a result of the electron transfer process, a depletion layer forms at the surface of the photocatalyst, during which in turn the band edges align to the water redox potentials. The band edge alignments at the surface/medium interface directly characterize light absorption as well as the energy state of the photogenerated charge carriers, and eventually catalytic reactions at the surfaces. Therefore, in order to properly comprehend the photocatalytic water splitting reactions in an operating environment, the aqueous environment-dependent band edges of various photocatalytic materials need to be primarily understood.

For years, in the first-principles density functional theory (DFT) studies, the environment-dependent band edge positions have been explored with slabs prepared with a vacuum layer. But, the surface environments are varied with different adsorbates species [155-157], their coverage [156], surface stoichiometry [148], and surface orientations [146, 158-160]. The calculated \( E_C \) or \( E_V \) of the different surface configurations relative to the \( \text{H}^+ / \text{H}_2 \) or \( \text{H}_2\text{O} / \text{O}_2 \) levels (referenced to the absolute vacuum level), show whether the HER or OER is feasible. That is based on the idea that if the charge carriers generated by light absorption have energy enough to trigger the reaction energy level (\( \text{H}^+ / \text{H}_2 \) or \( \text{H}_2\text{O} / \text{O}_2 \)), the reaction occurs. However, this idea is based on the assumption that the band edge positions of a material stays the same before and after contact with the electrolyte; therefore, the band edges measured in vacuum can
represent those in an operating environment. Yet, this assumption is incorrect because the band edges before and after contact with the electrolyte are different in many systems, as shown in Figure 4-23.

Figure 4-23 shows the conduction and valence band edge positions of various transition metal oxides (TMOs) experimentally measured in vacuum state (red lines, with UPS (ultraviolet photoelectron spectroscopy) measurement) and in an aqueous solution (black lines, with flat band potential measurement). Even at a glance, there is a big discrepancy between the band edges measured in vacuum and in an aqueous solution. This means the surface states as well as their band edges in vacuum are no longer the same as the states in contact with electrolyte even in the experimental conditions, suggesting a huge environmental effect on the band edge positions. Also, taking a close look at Figure 4-23, it is found that the band edge positions in an aqueous solution relative to the positions in vacuum are implicated in the intrinsic semiconducting nature of a material. In more specific, n-type semiconducting (or insulating) materials including Ta$_2$O$_5$, TiO$_2$, WO$_3$ and V$_2$O$_5$, have shown the upward shift in the band edges in water compared to those in vacuum, while CoO, FeO, NiO, MnO, CuO, Cu$_2$O, Co$_3$O$_4$ and Cr$_2$O$_3$, known as p-type semiconductors, move the band edges downward in water compared to the measurement in vacuum. This movement is in a similar vein as energy bands bending upward at the surface of n-type semiconductors in an aqueous solution deviating from bulk phase [24,153]. In contrast, p-type semiconductors present downward band bending in water, as a result of electron transfer in the process of electrochemical potential equilibrium between the semiconductor and water [23]. These two findings in Figure 4-23 imply that the band edge positions (energy states) calculated with a vacuum layer are similar to intact bulk states without much perturbation from the electrolyte (water in this study) (Figure 4-1). On the contrary, the band edges measured in an aqueous solution diverge from the intact bulk state because of a significant perturbation from water [23]. Accordingly, the band edges measured in vacuum cannot capture the electron transfer and band bending phenomena occurring at the real material/water interface. To reproduce the band edges in an aqueous environment, the solvation effect of water need to be included in DFT calculations.
Figure 4-23 Experimental conduction and valence band edges relative to $H^+/H_2$ of CoO, FeO, NiO, MnO, CuO, Cu$_2$O, Co$_3$O$_4$, Cr$_2$O$_3$, TiO$_2$, Ta$_2$O$_5$, WO$_3$, V$_2$O$_5$ measured with ultraviolet photoelectron spectroscopy (UPS) in vacuum state (red filled and open circles) [137,102, 161-163] and measured from flat band potential in an aqueous solution (black filled and open circles) [1,10,22,139,141,164-167] at pH = 1. ‘R’ and ‘A’ in parenthesis denote ‘rutile’ and ‘anatase’. The horizontal dashed lines are hydrogen and oxygen evolution potential levels, $H^+/H_2$ and $H_2O/O_2$.

Recently, a polarization continuum model (PCM) [168-169] has been reported, which implicitly models the solvation effect by placing a quantum-mechanical solute in a cavity surrounded by a continuum dielectric description of the solvent. This implicit solvation model has been expected to be a technique for understanding solute/solvent interfaces, economically calculating surface energy, reaction barrier and molecular solvation energies comparable to experimental values. However, the band edge positions calculated in the implicit solvation barely showed differences from those calculated with vacuum level reference [146, Section 4.1.4]. Furthermore, they have not correctly predicted the band edges measured from flat band potential as shown in Figure 4-23. This means that the implicit solvation calculation method fails to reproduce the experimental band edge realignments in an aqueous solution, because the model is unable to describe the real electron exchange occurring at the realistic surface/water interface. Thus, it is clear that the experimentally measured band edge positions in an aqueous solution are difficult to be reproduced without explicit water contact.

Y. Wu et al. [60] pioneered an explicit solvation method to assess the band edge positions at a material/aqueous solution interface, which successfully reproduces the values close to the experimental measurements of various materials. Nevertheless, they mostly studied paramagnetic materials which do not
require to care about complex magnetic configuration and a Hubbard $U$ correction parameter ($U_{\text{eff}}$) for the explicit solvation calculation. Also, they studied mainly non-oxide systems except for TiO$_2$ and WO$_3$, even though many metal oxides are regarded as good water oxidizing photocatalysts. The systematic study on both paramagnetic and magnetic metal oxides is still needed in the explicit solvation method because many magnetic metal oxides including CoO, Co$_3$O$_4$, FeO, Fe$_2$O$_3$, NiO, MnO and Cr$_2$O$_3$, as well as non-magnetic metal oxides such as TiO$_2$ and WO$_3$, have been taken into account as the potential co-catalyst for photocatalytic OER or HER.

We herein confirm using DFT calculations that the band edge positions are largely different in vacuum and in water as observed in the experiments, by comparing band edge positions of antiferromagnetic (AFM) CoO and paramagnetic rutile TiO$_2$ model systems calculated with a vacuum layer and with explicit water, independently. Based on the results, we demonstrate that explicit water contact is necessary in order to accurately assess the band edges in an aqueous solution in which photocatalysis occurs as well as to fundamentally understand the material/water interface. Moreover, we suggest optimal explicit solvation calculation methods by focusing on the effect of spin polarization and $U_{\text{eff}}$ values on the band edges of CoO and rutile TiO$_2$ model systems. At the end of this study, we verify the optimized methods by extending to other various materials including magnetic CoO, FeO, NiO, MnO as well as anatase TiO$_2$, WO$_3$, V$_2$O$_5$. We expect the optimized methods will help explicit solvation calculation be readily and economically conducted, but be closer to the experimental values.

4.3.2 Model system and structure preparation

4.3.2.1 Model system selection

TiO$_2$ is a prime candidate for photocatalysis and is currently almost the only material suitable for industrial applications [170], because of its abundance, photostability and superior activity. In particular, a high photocatalytic activity for HER or OER primarily originates from a band gap (~3 eV for stoichiometric TiO$_2$), and appropriate band edges relative to water redox potential [10,22,164,165]. More importantly, TiO$_2$ modulates the band gap as well as the band edge alignments to water redox potentials, with the formation of surface oxygen vacancies [148,171].

CoO nanoparticles of 2.4 - 2.6 eV band gap, were reported to be able to evolve stoichiometric H$_2$ and O$_2$ (2:1) from water splitting under visible light irradiation even without external driving potential or co-catalyst in neutral water [1], unlike bulk CoO phase. The CoO nanoparticles hit the record for the highest photocatalytic efficiency among the monolithic nano-particulate photocatalysts. This improvement in the photocatalytic properties of CoO nanoparticles relative to bulk phase comes from the optimal band edge
positions relative to water redox potential levels [1]. Our previous study demonstrated that the optimal band edge positions are mainly relevant to the specific facets on the nanoparticles which do not exist on larger-sized micropowders (Section 4.1).

Given not only that both TiO$_2$ and CoO exhibited superior photocatalytic properties with optimal band edge alignments to water redox potentials, but also that the optimal band edges were elucidated in detail to come from specific surface environments, both systems are considered appropriate model systems for this study.

**4.3.2.2 Bulk structure**

Bulk rutile TiO$_2$ was modeled with DFT and DFT + Hubbard $U$ (DFT + $U$) using VASP [43-44] with projected augmented wave (PAW) pseudopotentials from the VASP database and the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) to describe the exchange-correlation effects [45]. $U_{\text{eff}} = 2.5 - 12$ eV [172] were employed for Ti atoms in the DFT + $U$ calculation. An energy cutoff of 600 eV, a Gaussian smearing width of 0.05 eV, and a $6 \times 6 \times 8$ Monkhorst-Pack k-point mesh are used for the structural relaxations of rutile TiO$_2$ until all forces are less than 0.005 eV/Å. However, the DFT-relaxed TiO$_2$ bulk phase underestimated the experimental band gap (3 eV [144-145]) even with the correction of $U_{\text{eff}}$ (Figure 4-24(a)).

Bulk CoO crystallizes in the rock salt structure, experimentally, ground-state exhibits type-II antiferromagnetic (AFM-II) spin ordering [40-42]. To model the ground state magnetic ordering and electronic structure of bulk CoO, DFT + $U$ calculations are performed with PAW and GGA-PBE to address the strongly correlated and localized 3$d$ shell of Co with $U_{\text{eff}} = 1 - 6$ eV. An energy cutoff of 800 eV and a $6 \times 6 \times 6$ Monkhorst-Pack k-point mesh are used. Atom positions are relaxed until all forces are less than 0.005 eV/Å. The prepared AFM-II phases of bulk CoO with $U_{\text{eff}} = 4.1 - 5$ eV gives a band gap of 2.3 $- 2.66$ eV and lattice constant of 4.26 $- 4.264$ Å, in reasonable agreement with the experimental values of 2.4-2.6 eV [1,10,173] and 4.262 Å [46-49] for CoO (Figure 4-24(b) and Figure 3-1).
Figure 4-24 Graphs of band gap versus of $U_{\text{eff}}$ of bulk (a) rutile TiO$_2$, rock salt (b) CoO (c) FeO (d) NiO (e) MnO, (f) anatase TiO$_2$, (g) monoclinic WO$_3$ (h) orthorhombic V$_2$O$_5$. The horizontal dashed line in each graph denotes the experimental band gap of the material. ‘R’ and ‘A’ in parenthesis of (a) and (f) denote ‘rutile’ and ‘anatase’.

Bulk FeO, NiO and MnO have a crystal structure similar to CoO, rock salt and AFM-II magnetic ordering. To model the bulk FeO, NiO and MnO, DFT + $U$ calculations are performed as bulk CoO was modeled, but with $U_{\text{eff}} = 0 - 7.5, 0 - 8$ and $0 - 20$ eV for Fe, Ni and Mn. An energy cutoff of 800 eV and a $6 \times 6 \times 6$ Monkhorst-Pack k-point mesh are used. Atom positions are relaxed until all forces are less than 0.005 eV/Å. The obtained band gaps are 2.48 eV for FeO with $U_{\text{eff}} = 6.5$ eV, and 3.54 eV for NiO with $U_{\text{eff}} = 6.2$ eV, in good agreement with the experimental values of 2.5–2.6 eV and 3.6 eV for FeO [10] and NiO [10,102,164] (Figure 4-24(c) and (d)). However, the DFT-relaxed MnO bulk phase underestimates the experimental band gap (3.6 eV [10]) even with the Hubbard $U$ correction with large $U_{\text{eff}}$ value (Figure 4-24(e)).

Bulk WO$_3$ (monoclinic), V$_2$O$_5$ (orthorhombic) and anatase TiO$_2$ were also constructed with DFT + $U$ and GGA-PBE as rutile TiO$_2$ was modeled except for different $U_{\text{eff}} = 0 - 8, 0 - 8$ and $0 - 12$ eV for W, V and Ti atoms, and a $6 \times 6 \times 6$, a $6 \times 2 \times 5$, and a $6 \times 6 \times 2$ Monkhorst-Pack k-point mesh for WO$_3$, V$_2$O$_5$, and anatase TiO$_2$, respectively. The band gap of V$_2$O$_5$ calculated with $U_{\text{eff}} = 6.6$ is 2.8 eV (Figure 4-24(h)), the band gap of anatase TiO$_2$ with $U_{\text{eff}} = 8$ eV is 3.14 eV (Figure 4-24(f)), in good agreement with
the experimental values of 2.8 eV for V$_2$O$_5$ [102] and 3.2 eV for anatase TiO$_2$ [144-145,164]. However, the DFT-relaxed WO$_3$ bulk phase underestimates the experimental band gap (2.6 eV [102,164]) even with the correction with large $U_{\text{eff}}$ value (Figure 4-24(g)).

4.3.2.3 Surface structure

To study the band edge positions of rutile TiO$_2$ referenced to absolute vacuum level, we modeled symmetric TiO$_2$(110) ($1 \times 2$) slabs because rutile TiO$_2$ is known to favor to have (110) facets with the lowest surface free energy [174-177]. Since surface oxygen stoichiometry is sensitive to the sample preparation conditions in experiment [171], which results in the variation of the band edge positions of the surfaces, surface oxygen vacancy concentration varies from 0, to 0.5 and 1. For the structural relaxations of the slabs, all computational parameters were fixed as bulk TiO$_2$ was constructed with a vacuum layer of ~15 Å and a $8 \times 2 \times 1$ Monkhorst-Pack k-point mesh.

The band edge positions of CoO surfaces in vacuum were examined with symmetric supercells of various surface configurations which were verified to be present in different oxidation condition (Section 4.1); metal Co decorated CoO(111) (Co/CoO(111)), fully hydrogenated CoO(111) (H*-CoO(111)), clean CoO(100), fully hydroxylated CoO(111) (OH*-CoO(111)), together with bare CoO(111) for comparison. The detailed modelling method is introduced in Section 4.1.

We modeled the (001)-oriented symmetric slabs of FeO, NiO, MnO, WO$_3$, V$_2$O$_5$ because the (001) plane is expected to be favorable due to charge balance and the closely packed nature of the cleavage plane [178,179], as well as (001) oriented surfaces are frequently observed in the experiments for the FeO [178,180], NiO [178,181-183], MnO [178,184], WO$_3$[185-186], V$_2$O$_5$ [187] systems. In all cases, a vacuum layer of ~15 Å, a $6 \times 6 \times 1$ Monkhorst-Pack k-point mesh is used except for V$_2$O$_5$ ($6 \times 2 \times 1$). A type-II antiferromagnetic (AFM-II) configuration is initially constructed in slab structures of FeO, NiO, MnO as modeled for bulk phases, then the magnetic configuration is allowed to evolve during the structural optimization.

We modeled symmetric anatase TiO$_2$(101) ($2 \times 1$) slabs because anatase TiO$_2$ is known to favor having (110) facets with the lowest surface free energy [188-191]. For the structural relaxations of the slabs, all computational parameters are fixed as bulk anatase TiO$_2$ was constructed with a vacuum layer of ~15 Å and a $2 \times 6 \times 1$ Monkhorst-Pack k-point mesh.
4.3.3 On-site Coulomb interaction in TMOs

The 3d transition metal oxides (TMOs) show a variety of electronic and magnetic properties, ranging from insulating to metallic or even superconducting behavior, and from Pauli paramagnetism to ferromagnetism or antiferromagnetism. Additionally, these materials can often be tuned from one electronic or magnetic phase to another by varying the temperature, pressure, or doping. These various properties are mainly influenced by 3d orbitals forming d-bands with characteristic effective masses and different strengths of on-site Coulomb interactions. Since these 3d orbitals influence the band gap and the band edge positions [192-194], the 3d TMOs also have manifold optical properties or photocatalytic activities depending on the d-band characteristics. In practice, to interpret the diverse phenomena in the 3d TMOs, a Hubbard model [195-198] in which the electrons localized on d or f orbitals are subject to an additional on-site Coulomb interaction term (U) and site exchange term (J), has been used. Thus, a Hubbard correction parameter ($U_{\text{eff}} = U - J$) is particularly important to correctly understand the photocatalytic behaviors of various TMOs. Therefore, we herein find an optimal $U_{\text{eff}}$ value (and magnetic configuration) to estimate the $E_C$ of TMOs comparable to the experimentally measured values both in vacuum and in an aqueous solution.

4.3.4 $E_C$ in vacuum

The band edge positions of a material at the surface/water interface are determined by how the band edges deviate from those in the bulk phase. The deviation comes from the difference between the electrochemical potentials of electrons (i.e., the Fermi level) in the solid and the water. Thus, we examine the Fermi level (referenced to the absolute vacuum level) with respect to the on-site Coulomb interaction parameter ($U_{\text{eff}}$) for TMOs to determine the effect of $U_{\text{eff}}$ on the band edge positions in vacuum.

4.3.4.1 Paramagnetic rutile TiO$_2$(110)

Figure 4-25(a) shows the computed Fermi levels relative to vacuum level (−work functions) of TiO$_2$(110) slabs with various surface oxygen stoichiometries and with different $U_{\text{eff}}$ values. As the figure shows, the Fermi level is essentially independent of $U_{\text{eff}}$ for a given surface, but varies significantly with the surface stoichiometry. This implies that $E_C$ and $E_V$ do not change significantly with variation of $U_{\text{eff}}$, but are sensitive to the surface stoichiometry. As shown in Figure 4-25(b), there is indeed little change in either $E_V$ or $E_C$ of rutile TiO$_2$(110) slabs in vacuum as a function of $U_{\text{eff}}$, while $E_V$, $E_C$, and $E_F$ move upward in the energy diagram as the oxygen vacancy concentration is increased. This trend is consistent with excess electrons on the surface due to the oxygen vacancies, which decreases the electron affinity and increases
the work function of the TiO₂(110) slab. The decrease in work function with the removal of surface oxygen has also been demonstrated with experimental UPS measurements of rutile TiO₂ [171].

The calculated band edge positions of the fully oxygen-terminated TiO₂(110) slabs are similar to the experimental values when $E_C$ is estimated by adding the experimental band gap ($E_{g}^{\text{expt}}$) to the DFT-calculated valence band edge, $E_V$ (blue triangles in Figure 4-25(b)). Considering that rutile TiO₂ prepared at ambient temperature and atmospheric pressure is known to have O-terminated (110) surfaces [176,199-200], the experimentally measured band edge positions of TiO₂ seem to arise from the stoichiometric surface. We note that using $E_C = E_V + E_{g}^{\text{expt}}$ to determine the conduction band edge is reasonable for TiO₂ in vacuum DFT-calculated $E_V$ of TiO₂ is very similar the $E_V$ obtained from GW calculations, as well as the experimental value measured in vacuum with UPS [201-203]. Therefore, even though DFT calculation failed to precisely predict the $E_C$ (or $E_g$) unlike GW calculation, DFT calculation seems to provide reasonable $E_V$ in vacuum condition. In addition, Figures 4-26(b)-(d) show that, for a given surface, the value of $E_C = E_V + E_{g}^{\text{expt}}$ is relatively insensitive to the change of the $U_{\text{eff}}$ (also see Figure 4-26) while the DFT+$U$ computed value of $E_C$ changes more significantly with $U_{\text{eff}}$. The figure also shows that the valence and conduction band edges of rutile TiO₂ in vacuum are consistent with experimental measurements when determined from DFT calculations without a Hubbard $U$ correction. Thus, applying $U_{\text{eff}}$ is not necessary for the accurately predicting $E_C$ of rutile TiO₂ in vacuum. We also note that the band gap of rutile TiO₂ estimated with DFT calculations is not in agreement with experiment even with $U_{\text{eff}}$ more than 10 eV (Figure 4-24(a)).

**Figure 4-25** (a) Fermi level ($E_F$) relative to absolute vacuum ($E = 0$) of O-terminated rutile TiO₂ with stoichiometric (Stoich), half coverage of O vacancies (Red-0.5), and full coverage of O vacancies (Red-1) surfaces computed with different values of $U_{\text{eff}}$ (no $U$, 2.5 and 4 eV). (b) $E_C$ and $E_V$ for the different surfaces.
computed with different values of $U_{\text{eff}}$. In Figures (b) – (d), $E_V$ and $E_C$ are relative to absolute vacuum. $E_C = E_V + E_{g}^{\text{expt}}$ indicates the value of $E_C$ determined by adding the experimental band gap to the computed valence band edge. The experimental value of $E_C$ measured for rutile TiO$_2$ in vacuum [102] is indicated by the horizontal green line).

**Figure 4-26** Valence and conduction band edges of full oxygen-terminated rutile TiO$_2$ surface (stoichiometric surface) in vacuum, with respect to $U_{\text{eff}}$. $E_V$ and $E_C$ are relative to absolute vacuum. $E_C = E_V + E_{g}^{\text{expt}}$ indicates the value of $E_C$ determined by adding the experimental band gap to the computed valence band edge, where $E_{g}^{\text{expt}}$ is the experimentally measured band gap. $E_{g}^{\text{DFT}}$ indicates the DFT-calculated band gap.

4.3.4.2 Antiferromagnetic CoO surfaces

Rock salt CoO is frequently observed to have a magnetic phase in bulk structure and nanoparticles [204]. Also, in most of CoO studies with DFT on the thermodynamic stability, AFM-II phase is the most stable than any other magnetic configurations for both bulk and surface structures. However, considering of its Néel temperature of 291 K [40], we expect that paramagnetic as well as antiferromagnetic phase can be formed for CoO at room temperature. Therefore, we consider a non-magnetic phase as well as an AFM-II phase for the prediction of the band edge positions of CoO in vacuum.

As observed in TiO$_2$(110) slabs in vacuum (Figure 4-25(a)), the Fermi level changes with surface chemistry, but for a given surface, neither spin polarization nor the value of $U_{\text{eff}}$ leads to significant changes, except for the large fluctuation for CoO(100) (Figure 4-27(a)). Therefore, one might expect that the band edge positions are also similar regardless of the spin polarization and $U_{\text{eff}}$. However, Figure 4-27(b) and (c) show that the $E_V$ and $E_C$ change significantly with the use of spin polarization + $U_{\text{eff}}$, shifting upward more
than 2 eV. This significant change suggests that the effects of spin polarization and $U_{\text{eff}}$ on band edge positions in vacuum are in fact very large.

The band edge positions estimated with spin polarization + $U_{\text{eff}}$ (Figure 4-27(c)) have similar values of $E_C$ to those estimated by adding the experimental band gap to the computed $E_V$, $E_C = E_V + E_{g\text{expt}}$. This is possible because the calculated band gap size of all CoO surfaces with AFM-II+$U_{\text{eff}} = 4.1$ eV ($2-2.6$ eV) is comparable to the experimental value ($2.4-2.6$ eV).

Among the various surfaces in Figure 4-27(c), a CoO(100) slab exhibits $E_V$ and $E_C$ similar to those measured from the experiment. Based on the experimental and theoretical reasons that CoO(100) facet thermodynamically tends to exist in high vacuum state of $\sim 10^{-10}$ Torr ($\sim 1.315 \times 10^{13}$ atm, $\Delta \mu_O = \sim 0.5$ in Figure 4-3) in which UPS measurement was performed for the $E_C$ and $E_V$ examination of CoO [102], we guess the $E_V$ and $E_C$ of CoO in vacuum come from CoO(100) surface with an AFM-II phase. Also, considering that CoO tends to be cleaved and exposed to (100) plane [72,136], CoO(100) is considered as the most probable surface configuration for CoO.

**Figure 4-27 (a)** Fermi energy levels relative to absolute vacuum ($E = 0$) of Co/CoO(111), H*-CoO(111), CoO(100), OH*-CoO(111) and bare CoO(111) slabs computed using DFT with and without spin polarization and/or $U_{\text{eff}} = 4.1$ eV. **(b)** Conduction and valence band edge positions ($E_C$ and $E_V$) without spin polarization and without $U_{\text{eff}}$. **(c)** $E_C$ and $E_V$ with the AFM-II phase and $U_{\text{eff}} = 4.1$ eV. In Figures (b) and (c), $E_V$ and $E_C$ are relative to absolute vacuum. $E_C = E_V + E_{g\text{expt}}$ is the $E_C$ determined by adding the experimental band gap to the computed $E_V$. The experimental value of $E_C$ measured for CoO in vacuum [102] is indicated by the horizontal green line).
4.3.5 $E_C$ in water

4.3.5.1 Antiferromagnetic CoO surfaces

To predict the band edge positions of CoO surfaces in an aqueous solution, we use an approach similar to the three-step method introduced in Ref. 60. The approach directly investigates the position of the conduction band edge of a material relative to the water reduction potential ($H^+/H_2$) level, which is determined by three energy values of (1) bulk CoO, (2) bulk liquid water, and (3) CoO/water interface as schematically illustrated in Figure 4-13. The values for the first and third steps (bulk CoO and CoO/water interface) can be affected by spin polarization (AFM-II in this study) and $U_{\text{eff}}$ values since they contain 3d shell Co atoms in the calculations.

4.3.5.1.1 $E_C$ of bulk CoO relative to Hartree potential level

Spin polarization and $U_{\text{eff}}$ considerably vary $E_C^{\text{CoO(bulk)}} - H^{\text{CoO(bulk)}}$ in bulk CoO (1$^{\text{st}}$ step value), as shown in Figure 4-28. The increment from the no spin polarization + no $U$ calculation (the very left) to the AFM-II + $U_{\text{eff}} = 6$ eV calculation (the very right) is almost 4 eV, which might potentially distort the $E_C$ vs. $H^+/H_2$ at the end of the three step calculation. Nevertheless, if the 3$^{\text{rd}}$ step value ($H^{\text{CoO(interface)}} - H^{\text{water(interface)}}$), i.e., potential drop at the CoO/water interface, also changes by the same amount as the 1$^{\text{st}}$ step value changes with AFM-II and/or $U_{\text{eff}}$ value, the $E_C$ vs. $H^+/H_2$ determined by the relative values of the three steps would be similar, independent of the spin polarization and/or $U_{\text{eff}}$ value.
Figure 4-28 $E_{CoO}^{CoO(bulk)} - H_{CoO(bulk)}$ value (the 1st step value in the three step method [60]) of bulk CoO with and without spin polarization and various $U_{eff}$ values.

4.3.5.1.2 Potential drop at CoO/water interface

Figure 4-29(b) shows plots of average Hartree potential in CoO(100) slab/water supercell as a function of distance along the $z$-axis (height axis) (Figure 4-29(a)), showing potential drops at the interface (the 3rd step value) with various conditions of spin polarization and/or $U_{eff}$ values. Only the plot of Hartree potential computed with no spin polarization + no $U_{eff}$ calculation (Figure 4-29(c)) shows the perfect stair-like Hartree potential change between the CoO surface and water regions along the distance (ideal plot). Yet, the plots with other conditions (from no spin polarization + $U_{eff} = 4.1$ to AFM-II + $U_{eff} = 4.1$) diverge from the ideal plot. The deviations are not as large as the change in the 1st step values (Figure 4-28), as shown in tables in Figures 4-30(d) and (e)), which implies that there is a huge effect of spin polarization + $U_{eff}$ on the $E_C$ vs. $H^+/H_2$ estimated from the three step calculation. However, a close look at the plots that show the least deviation from the ideal plot (Figure 4-29(d) and Figure 4-29(e)), gives us important information; if stair-like Hartree potential – distance plots could be obtained from the calculations with AFM-II and/or $U_{eff}$ values, the plots are similar to the ideal potential drop (Figure 4-29(c)). That means again the ideal potential drop at the interface of slab/water can be found without considerations of spin polarization and $U_{eff}$ even for the AFM-II CoO phase. Since the potential drop at the interface converges to the ideal value regardless of spin polarization and/or $U_{eff}$ value, the $E_C$ vs. $H^+/H_2$ estimated from the three step method will be solely affected by the $E_{CoO}^{CoO(bulk)} - H_{CoO(bulk)}$ (1st step value).
Figure 4-29 (a) Snapshot of the atomic distribution in CoO(100)/water interface supercell. Blue, red, and white circles denote Co, O, and H atoms, respectively. Planar-averaged Hartree potential of the CoO(100)/water interface computed for the structure shown in (a) along z-axis (b) with or without spin polarization and/or various $U_{eff}$ values, (c) without spin polarization + no $U_{eff}$ correction, (d) with AFM-II + no $U_{eff}$, (e) with AFM-II + $U_{eff} = 3$ eV. Dotted lines in (b)-(e) indicate macro-averaged Hartree potentials of the plot calculated with no spin polarization + no $U_{eff}$. For comparison, the plot of no spin polarization + no $U_{eff}$ (no spin-no $U$, black line) is superimposed in (d) and (e). Numbers in blue color in (d) and (e) denote the deviations from the ideal plot (black line). Tables in (d) and (e) show the 1st step values calculated with ‘no spin-no $U$’ and ‘AFM-II + $U_{eff}$’ and $\Delta$ indicates the difference between the two values.

4.3.5.1.3 $E_{C}$ vs. $H^{+}/H_{2}$ of CoO surfaces

Figure 4-30 shows $E_{C}$ vs. $H^{+}/H_{2}$ of bulk CoO and CoO surfaces calculated using the three step method with various conditions of spin polarization and/or $U_{eff}$ values, by constraining the potential drop at the interface (3rd step value) to the ideal value (Figure 4-29(c)). As can be seen in Figure 4-30, the $E_{C}$ vs. $H^{+}/H_{2}$ is very different depending on spin polarization and/or $U_{eff}$ values, which shows that the explicit solvation calculation for a magnetic phase is very notorious for the prediction of its band edge positions. Except for the no spin polarization + no $U_{eff}$ calculation (‘no spin-no $U$’ in Figure 4-29), the estimated $E_{C}$ vs. $H^{+}/H_{2}$ are far from the realistic range; The bulk CoO calculated with no spin polarization + no $U_{eff}$, shows $E_{C}$ vs. $H^{+}/H_{2}$ comparable to the experimental values of bulk CoO [1,10] and CoO micropowders [1]. In addition, OH*-CoO(111) surface releases $E_{C}$ vs. $H^{+}/H_{2}$ similar to that of CoO nanoparticles in
experiments [1]. As demonstrated in our previous study in Section 4.1, the presence of the OH*-CoO(111) facet on the CoO nanoparticles is the origin of the upward shifted $E_C$ in CoO nanoparticles compared to the bulk CoO.

Considering that Co atoms in the CoO surface in contact with water lost their magnetic moments (Figure 4-11), it is reasonable to carry out the explicit solvation calculation on the CoO/water interfaces without consideration of spin polarization. In addition, even though $U_{\text{eff}}$ was applied to the Co atoms in the explicit solvation calculation, the interaction of water with the CoO surface significantly broadened the DOS of Co 3$d$ orbitals. This directly suggests that the 3$d$ orbitals are not entirely localized in contact with water, inducing delocalization of $d$-band splitting. [205, Figure 4-12]. Accordingly, an explicit solvation calculation with no spin polarization + no $U_{\text{eff}}$ is enough to capture the realistic CoO/water interfacial structure, charge transfer between the CoO and water, band bending aspect, and band edge alignment to water redox potentials.

Figure 4-30 Conduction band edge position ($E_C$) relative to water reduction potential ($H^+/H_2$) of bulk CoO, Co/CoO(111), $H^*$-CoO(111), CoO(100), OH*-CoO(111) and CoO(111) surfaces estimated with three step method, with fixed value (ideal value) of the potential drop at the CoO/water interface. The water contact with bulk CoO is done by cleaving the relaxed bulk structure perpendicular to (001) plane [75]. Yellow and orange horizontal double lines are the $E_C$ of CoO nanoparticle [1] and bulk CoO (or micropowder [1]) obtained with flat band potential measurements at pH = 7.
4.3.5.2 Paramagnetic rutile TiO$_2$(110)

In this section, we further discuss why $U_{\text{eff}}$ correction is no longer needed for the realistic prediction of the band edge positions of TMOs in an aqueous environment, using paramagnetic rutile TiO$_2$. Figure 4-31 shows $E_C$ vs. H$^+/H_2$ of bulk TiO$_2$ and TiO$_2$(110) surfaces with various surface oxygen stoichiometry, calculated from the three step approach. As done for CoO in Figure 4-29, we fixed the potential drop at the interface to the ideal value obtained from no $U_{\text{eff}}$ calculation. The bulk TiO$_2$ has the lowest band edge position, while it increases gradually from stoichiometric to half- and full-surface oxygen vacancy generated TiO$_2$(110) surfaces in sequence. This makes sense because when oxygen vacancy leaves the lattice, it keeps back excess electrons, making the surface negatively charged. This negatively charged surface readily grants the excess electrons to the adjacent water due to the electrochemical potential difference between the surface and water, increasing the degree of upward band bending at the TiO$_2$ ($n$-type) surface. Accordingly, the $E_C$ vs. H$^+/H_2$ shifts upwards as the surface reduces and this trend is in agreement with the change in $E_C$ in vacuum (Figure 4-25).

![Figure 4-31 Conduction band edge positions ($E_C$) relative to water reduction potential (H$^+/H_2$) of cleaved bulk TiO$_2$ and TiO$_2$(110) surface with full surface oxygen ((110)-stoi), half surface oxygen vacancy ((110)-red-0.5), full surface oxygen vacancy ((110)-red-1) and variation of $U_{\text{eff}}$ (no $U$, 2.5 and 4 eV) calculated from three-step calculation. For comparison, the experimental value of the $E_C$ vs. H$^+/H_2$ of TiO$_2$ measured from flat band potential in an aqueous solution of pH = 1 [10] is superimposed in the figure (horizontal orange line).](image)
As we observed in CoO, $U_{\text{eff}}$ correction is also detrimental to the accurate evaluation of $E_C$ vs. H$^+$/$\text{H}_2$ of rutile TiO$_2$ with the explicit solvation method, because $U_{\text{eff}}$ correction varies the first step value of bulk TiO$_2$ ($E_C^{\text{TiO}_2} - H^{\text{TiO}_2}$) up to $\sim$ 0.9 eV as shown in Figure 4-32. This variation of the first step value keeps the $E_C$ far from the experimental values in all surfaces. Only no $U_{\text{eff}}$ correction provides $E_C$ vs. H$^+$/$\text{H}_2$ of rutile TiO$_2$ closest to the experimental measurement. Therefore, $U_{\text{eff}}$ correction is also no longer needed for the band edge position evaluation in the explicit solvation, even for paramagnetic TiO$_2$.

**Figure 4-32** (a) $E_C$ — Hartree potential of bulk rutile TiO$_2$ (the 1$^{\text{st}}$ step value in the three step approach) with respect to $U_{\text{eff}}$. (b) Planar-averaged Hartree potential of the rutile TiO$_2$(110)/water interface with variation of $U_{\text{eff}}$ value. The blue number in Figure (b) denotes the maximum deviation from the ideal Hartree potential plot of the TiO$_2$(110)/water interface.

### 4.3.6 Optimal conditions for $E_C$ vs. H$^+$/$\text{H}_2$

Table 4-5 summarizes $E_C$ and $E_V$ relative to H$^+$/$\text{H}_2$ level of rutile TiO$_2$ and CoO model systems calculated with vacuum reference and with explicit solvation method, together with their experimentally measured values. For simplicity, among DFT-calculated $E_C$ and $E_V$ of various surfaces under the various conditions that are considered in this study, only conditions showing band edges closest to the experimental values are summarized in the table.

In common, for rutile TiO$_2$ and CoO, the $E_C$ in vacuum can be accurately predicted by adding the experimental band gap to the $E_V$ relative to absolute vacuum level ($E_C = E_V + E_g^{\text{expt}}$) rather than the direct reading of $E_C$. This is because the DFT-calculated $E_V$ for both TiO$_2$ and CoO presented accurate level comparable to the experiment. Since the calculated $E_V$ of rutile TiO$_2$ (110) barely changes with variation of
$U_{\text{eff}}$ value (Figure 4-26), the $E_C$ estimated from $E_V + E_g^{\text{expt}}$ also does not vary much. Therefore, Hubbard $U$ correction is unnecessary for the accurate prediction of $E_C$ for rutile TiO$_2$, although Hubbard $U$ correction improves the accuracy of the calculated band gap (Figure 4-26). However, for CoO, the calculated $E_C$ and $E_V$ of CoO in vacuum exhibit the values closest to the experiment only when DFT calculation is conducted on CoO(100) surface with spin polarization (AFM-II) + $U_{\text{eff}} = 4.1$ eV. Therefore, $E_C$ and $E_V$ of TMOs in vacuum can be precisely estimated with the combination of appropriate surface orientation, magnetic ordering configuration and strength of the on-site Coulomb interaction ($U_{\text{eff}}$). The optimal conditions are different depending on materials.

However, the $E_C$ and $E_V$ of rutile TiO$_2$ and CoO model systems in an aqueous solution can be best fitted without $U_{\text{eff}}$ correction and without spin polarization as can be seen in Table 4-5. This means that the explicit calculation on the surface/water interface without spin polarization and without $U_{\text{eff}}$ correction, can capture the realistic electron transfer as well as the band alignment phenomena at the interface of the TiO$_2$ (or CoO)/water without distortion. Therefore, we can expect economical explicit solvation calculation compared to other expensive explicit calculation methods, but accurate prediction of band edge positions comparable to the experiment.

Unlike the vacuum referenced calculation of $E_C$, the $E_C$ vs. $H^+/H_2$ of rutile TiO$_2$ and CoO model systems in an aqueous solution can be directly assessed from the three step approach with the explicit water contact. This is possible because the explicit solvation involves the real electron transfer across the semiconducting material/water interface, which directly releases $E_C$ of the material relative to $H^+/H_2$ of water [60]. Instead, $E_V$ can be computed by $E_V = E_C - E_g^{\text{expt}}$ under the assumption that the $E_C$ estimated from water contact calculation is relatively accurate. This is not only because the $E_C$ and $E_V$ predicted with the relationship are closer to the experimental value regardless of the accuracy of the DFT-computed band gap size, but also because the main charge transfer between the material and polar water molecules are electrons.

<table>
<thead>
<tr>
<th></th>
<th>Vacuum</th>
<th>Water (at pH = 7)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_C$ vs. $H^+/H_2$</td>
<td>$E_V$ vs. $H^+/H_2$</td>
</tr>
<tr>
<td>Rutile TiO$_2$ (exp.)</td>
<td>0.10</td>
<td>3.50$^{[102]}$</td>
</tr>
</tbody>
</table>

Table 4-5 Conduction and valence band edge positions relative to $H^+/H_2$ ($E_C$ and $E_V$ vs. $H^+/H_2$) of TiO$_2$ and CoO model systems calculated with vacuum level reference (vacuum) and explicit solvation method (water) with $U_{\text{eff}}$ correction or spin polarization. For comparison, the experimental values measured with UPS in vacuum and with flat band potential in an aqueous solution are also summarized. The negative $E_C$ value denotes the conduction band edge above $H^+/H_2$. The unit is V (vs. NHE). Rutile TiO$_2$ and CoO prepared in the present study are marked with green shade.
<table>
<thead>
<tr>
<th>Material</th>
<th>$E_{\text{C}}$ vs. $H^+$/H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk TiO$<em>2$ – no $U</em>{\text{eff}}$</td>
<td>—</td>
</tr>
<tr>
<td>TiO$<em>2$ (110) – any $U</em>{\text{eff}}$ values</td>
<td>-0.19  2.81</td>
</tr>
<tr>
<td>CoO (exp.)</td>
<td>-1.70  0.70 [102]</td>
</tr>
<tr>
<td>Bulk CoO – no spin + no $U_{\text{eff}}$</td>
<td>—</td>
</tr>
<tr>
<td>CoO(100) – AFM-II + $U_{\text{eff}} = 4.1$ eV</td>
<td>-1.89  0.71</td>
</tr>
</tbody>
</table>

### 4.3.7 Validation of optimized conditions

The above optimized conditions for the prediction of band edge positions in vacuum and in an aqueous solution are further validated on FeO, NiO, MnO, anatase TiO$_2$, WO$_3$ and V$_2$O$_5$ as shown in Figure 4-33. In all cases, the calculated $E_{\text{C}}$ vs. $H^+$/H$_2$ are comparatively in good agreement with the experimental measurements, except for the vacuum reference calculation of V$_2$O$_5$ and WO$_3$. The discrepancy seems to stem from the inaccurate DFT-estimated $E_{\text{V}}$ or from the misunderstanding of the stable surface configurations in the vacuum state. Most importantly, we confirm here again 1) band edges in vacuum are different from those in an aqueous solution both in the experimental measurement and computational study. 2) with optimal conditions with $U_{\text{eff}}$ correction or magnetic ordering, which predicts the accurate $E_{\text{V}}$ with a vacuum layer, DFT calculations can reproduce the real experimental band edge positions in vacuum regardless of the accuracy of band gap. In most cases, the optimal conditions can be found from the parameters that describe the experimental band gap of bulk phase of a material (Figure 4-24). 3) the explicit solvation calculations without consideration of on-site Coulomb interaction + spin polarization, can assess the realistic band edges of TMOs in an aqueous solution.
Figure 4-33 Conduction band edge positions of CoO, FeO, NiO, MnO, rutile TiO$_2$, anatase TiO$_2$, WO$_3$, V$_2$O$_5$ experimentally measured (open symbol) and calculated with DFT (filled symbol) in vacuum (blue) and in an aqueous solution (red). The band edges of FeO, NiO in vacuum are calculated for (001) orientated surface, the band edges of anatase TiO$_2$ in vacuum are computed for (011) surface, with the conditions optimized for bulk phase that can have accurate experimental band gap and magnetic ordering (Figure 4-24(c), (d), (f)). Since an optimal $U_{\text{eff}}$ cannot be found for accurate experimental band gaps of MnO (Figure 4-24(e)) and rutile TiO$_2$ (Figure 4-24(a)), $U_{\text{eff}} = 0$ was applied to the MnO(001) and rutile TiO$_2$ (110) surfaces.

4.3.8 Summary

This study first argues and reveals the big discrepancy in the $E_V$ and $E_C$ of TMOs experimentally measured in vacuum and in an aqueous solution. To confirm the discrepancy, in the density functional theory (DFT) calculations, we find optimal conditions of spin polarization and/or on-site Coulomb interaction parameter ($U_{\text{eff}}$) for rutile TiO$_2$ and CoO model systems in vacuum and in an aqueous solution, independently; it is demonstrated that for vacuum reference calculation, appropriate $U_{\text{eff}}$ value, magnetic configuration and surface configuration should be identified. Moreover, $E_C$ in vacuum estimated from the $E_V + E_{\text{g} \text{expt}}$ is closer to the experimentally measured value (UPS measurement in vacuum), independent of the accuracy of band gap. For an explicit solvation method, spin polarization and $U_{\text{eff}}$ correction are no longer needed for the best fit to the experimental measurements. Also, the $E_C$ in an aqueous solution can be directly predicted with the explicit solvation method, while $E_V = E_C - E_{\text{g} \text{expt}}$ exhibits a value similar to the experiment in an aqueous solution (flat band potential measurement). It is demonstrated that the optimized parameters and evaluation methods for $E_C$ and $E_V$ in vacuum calculation and in the explicit water calculation, are in good agreement with the experimental measurements in other TMOs including FeO, NiO, MnO, anatase TiO$_2$, WO$_3$ and V$_2$O$_5$. We elucidated in this study that the explicit solvation calculation should be performed in order to understand the band alignment behavior of a material to water redox level in a real operating environment in which water splitting occurs. With the general DFT calculations of slabs with a vacuum layer, the potential photocatalytic capability for water splitting will never be able to be predicted unless materials intrinsically have similar band edge positions both in vacuum and in an aqueous solution such as TiO$_2$. We strongly believe that our work will be a milestone in offering the efficient and optimized explicit solvation methods for a variety of TMOs, for the prediction of the band edge positions and even for study of the semiconductor/water interfacial structures and properties.
4.4 Photocatalytic hydrogen evolution activity of Co/CoO(111) hybrid structure: Study on Co layer thickness effect

4.4.1 Motivation and objectives

Spontaneous solar-driven water splitting is a highly promising pathway for a clean and renewable energy supply in the future. The ultimate goal is to develop efficient, economical and stable photocatalysts which are able to accomplish overall water splitting under visible light irradiation, without using a sacrificial agent or external bias. Recently, cobalt-based materials have been highlighted as innovative solar-driven water splitting catalysts. It is because of their H₂ evolving ability [206-207], different from most cobalt-based materials which have been assessed as water oxidizing electrocatalysts in the past decade [208-215]. To date, CoO nanoparticles showed the highest solar-to-hydrogen conversion efficiency creating both H₂ and O₂ without external bias or a co-catalyst in neutral water. The overall water splitting on the CoO nanoparticles could be realized because three steps of photocatalysis [26] occurred spontaneously only under illumination: (i) A specific facet has optimal band edge positions relative to water redox potential for light absorption (Section 4.1), (ii) The photogenerated charge carriers are efficiently separated between two different kinds of facets on the nanoparticle (Section 4.1), (iii) the photogenerated charge carriers have energies high enough to overcome the kinetic barriers for H₂ and O₂ evolutions at the active facets (Section 4.1). However, this spontaneous photocatalysis on a monolithic material is observed in the very limited conditions of specific material, morphology, size and surface environment [Section 4.1-4.2,1,30-38].

In general, metal co-catalysts have been often deposited to promote HER activity through two steps: separating charge carriers by suppressing the electron-hole recombination in photocatalysts and serving as the reaction sites by lowering the kinetic barrier for HER. Metal Co formed on CoO nanoparticles with simple annealing in reducing environment, also lowered kinetic barrier for HER (HER overpotential) and improved electrochemical HER activity compared to pure CoO [89]. The enhancement in the HER activity was dependent on the thickness of the Co layer formed in the Co/CoO hybrid structures [89]. In particular, an optimal Co layer thickness in the Co/CoO hybrid structure exhibited very low HER overpotential comparable to the commercial Pt/C catalyst, together with much better long-term stability than pure CoO [89]. Nevertheless, the origins of the enhancement and the thickness dependency of the HER activity have not been clarified yet. Furthermore, it has not been studied whether the Co/CoO hybrid structures are photocatalytically active for hydrogen evolution from water cleavage.

In our previous study in Figure 4-14, it was suggested that CoO can improve its photocatalytic capability for HER with metal Co decoration. Co decoration shifts the band edges of the CoO layer to more negative potentials relative to H⁺/H₂, differently from those of bare CoO surface with positive potential (Figure 4-14), suggesting that Co decoration makes the CoO layer active for H₂ evolution under irradiation.
In addition to the photo-response of the semiconducting CoO layer, metal Co itself can induce the surface plasmon resonance (SPR) effect. This SPR effect occurs when metal nanoparticles with size much smaller than photon wavelength excite surface plasmons under illumination, and create electron-hole pairs of high energy called hot electron-holes. The SPR effect can be employed to deliver the hot carriers from the metal nanoparticle to the adjacent semiconducting (or insulating) substrate and to induce HER and/or OER on the hybrid structure from water splitting [216-218]. This effect is very important and interesting in photocatalysis of water, since it can trigger HER or OER even with large band gap materials (of UV spectrum) under visible light, with the transferred hot carriers from metal nanostructures. Our recent calculation demonstrated that Co has better capability to generate a higher population of hot electrons than Au [219], which is well-known material for SPR effect. However, how the SPR effect works in the metal Co layer formed on CoO, and which Co/CoO hybrid structure is optimal for photocatalytic hydrogen evolution, are unknown.

We herein study the photocatalytic behaviors of the Co/CoO hybrid structures with different Co layer thickness for H₂ evolution. The thickness-dependent interfacial structures/properties of the Co/CoO hybrid structures are identified by examining the electron transfer between the Co and CoO layers, band bending aspects in CoO layers and Schottky barrier height (SBH). We also investigate the two kinds of photo-response occurring in metal Co and semiconducting CoO layers as a function of Co layer thickness, independently: To evaluate the feasibility of photocatalytic HER on the Co/CoO hybrid structures by light absorption, we compare the conduction band edge position (E_c) relative to water reduction potential (H⁺/H₂), with the HER overpotential. For the investigation of the SPR effect in Co layers, the distribution of energy-population of hot electrons is calculated. Based on the thickness-dependent photocatalytic properties, we determine the optimal thickness of Co layer in the hybrid structures for active H₂ evolution from water splitting under light sources.

### 4.4.2 Co/CoO surfaces

Experimentally observed Co/CoO core-shell structured nanoparticles are manufactured by reducing CoO nanoparticles in pure Ar or Ar/H₂ mixture atmosphere [89]. The interface of the Co and CoO regions formed during the reducing procedure, showed smooth (111) plane matching between the Co and CoO layers [89]. To mimic the experimentally generated Co layers and the interface of the Co/CoO core-shell structure, we removed 1 ~ 4 oxygen atomic layers from both surface sides of the initial CoO(111) lattices. The created hybrid structure has a Co layer in the shell and a CoO layer in the core with a symmetric supercell as shown in Figure 4-34. To study the sole effect of Co layer thickness, the total number of CoO
layers was fixed with 5 Co and 4 O layers. We named each supercell Co(x)/CoO(111), where x is the number of atomic Co(111) layers formed on the CoO(111) core. For example, Co(4)/CoO(111) denotes a hybrid structure which has 4 atomic Co(111) layers on each shell layer in a symmetric supercell, together with a CoO(111) layer in the central region.

![Atomic configuration of Co(2)/CoO(111) symmetric supercell, relaxed with DFT calculation. This figure shows an example of atomic configuration of Co(x)/CoO(111) supercell relaxed with DFT calculation in this study.](image)

Figure 4-34  Atomic configuration of Co(2)/CoO(111) symmetric supercell, relaxed with DFT calculation. This figure shows an example of atomic configuration of Co(x)/CoO(111) supercell relaxed with DFT calculation in this study.

We modeled the Co/CoO(111) slabs using supercells of a (2 × 2) in-plane unit cell with 4 atoms in each layer. For the structural relaxations of the slabs, a vacuum layer of ~15 Å was constructed perpendicular to the surface. The atoms in the central 5 layers were fixed in the bulk CoO positions, while all other atoms were allowed to fully relax. AFM-II spin ordering was initially set in all slab structures with $U_{\text{eff}} = 4.1$ eV on Co atoms, a 6 × 6 × 1 Monkhorst-Pack k-point mesh.

### 4.4.3 Structures of Co layers

It has been widely believed that the characteristic of a heterointerface formed with two different materials is determined by the bulk characteristics of the two materials. Undoubtedly, a phase located far
away from the heterointerface will have the structure similar to its bulk phase. Yet, a variety of interesting and unexpected phenomena have been found to originate from the peculiar heterointerfaces in many systems [220-224]. The peculiar heterointerfaces might come from the interesting combination of two different materials, or from a heterointerfacial structure/property different from their bulk phases. In the case of epitaxial interface, the structures/properties are complex because various effects come from lattice mismatch (strain) between the adjacent materials.

A recent HRTEM (high resolution transmission electron microscopy) image [89] showed that Co/CoO core-shell hybrid structure prepared by reducing CoO nanoparticles, has a smooth lattice matching along the (111) plane at the interface of the Co and CoO layers. The lattice parameter of the Co layer is the same as the adjacent CoO lattice (~0.24 nm), which is largely different from the bulk value of the central Co core (~0.2 nm). This directly shows that the Co layer right next to the Co/CoO interface is epitaxial with the CoO layer, and the Co layer is subjected to very large in-plane strain, up to 20% tension.

In general, the very large strain due to lattice mismatch at the interface is accompanied by the structural defect formation for relaxing the strain. But, some HRTEM observations of metal/metal oxides heterojunction systems [225-230] manipulated with oxidation or reduction, exhibited high porosity together with an epitaxial metal/metal oxide interface, without forming other defects. Even for the Co/CoO(100) interface created from the oxidation of Co, an epitaxial structure is formed without defect formation at the interface [228,229], but with high porosity [231] as observed at the Co/CoO(111) interface [89]. Therefore, the formation of an epitaxial heterointerface at the Co/CoO(111) might be feasible in the very localized region with the assistance of the enormous pores for the strain relaxation, although we have not been able to imagine the epitaxial structure owing to the very large lattice mismatch between metal and oxide layers.

Figure 4-35(a) shows the atomic configurations of the DFT-relaxed Co/CoO(111) hybrid structures constructed from the removal of oxygen from the initial CoO(111) lattice. The relaxed structures describe the Co/CoO(111) shell/core structures which have CoO(111) in the core, Co(111) in the shell regions. All hybrid structures seem to have epitaxial structures with the underneath CoO layers as observed experimentally [89]. Thus, all Co layers have almost 20 % tensile strain along in-plane, as expected from the previous HRTEM image [89]. According to our MD studies of defect (Figure A-5-1 in the Appendix), aspect ratio (Figure A-5-2 to A-5-4 in the Appendix), size (Figure A-5-5 in the Appendix) effects on the stress-strain curves of Co, thin film of perfect lattice without defect, of low aspect ratio and of small size (similar to the Co thin layer in the Co/CoO core/shell nanoparticles) can have considerably improved elastic limit (elasticity) compared to bulk metal. This expectation was experimentally confirmed that the elastic limit and yield strength of Au nanowire [232] and sub-micron metallic glasses [233] significantly increase
by ~ 3−10 times compared to bulk phases. Hence, the metal Co layer formed on CoO nanoparticles may sustain the large lattice mismatch in local area without generating defects.

In addition to the severe in-plane strain in Co layers, to identify their structures along the out-of-plane axis, we investigate lattice parameter ratio of Co and CoO layers (a(\text{Co})/a(\text{CoO}) ratio) along the thickness direction as defined in the inset of Figure 4-35(b). There are three ideal values in the a(\text{Co})/a(\text{CoO}) ratio in this study. One is 0.579, when volume conserves even under the large in-plane strain of 20% (lower ideal value), which is an unrealistic case. The second is 0.782, when face-centered cubic (FCC) structured-Co follows Poisson’s ratio of \text{Co} = 0.31 [234] under elastic in-plane strain (middle ideal value). The final is bulk value, \text{i.e.,} 0.8333, when the Co layer is unstrained (upper ideal value). As can be seen in Figure 4-35(b), all the ratios in the Co/CoO(111) hybrid structures are between the lower and upper ideal values, and very close to the middle value. That means that the actual structural state of the interfacial Co layers is similar to the biaxially strained Co together with Poisson’s ratio. Therefore, the Co layers are present between the two ideal states as schematically depicted in Figure 4-35(c), which suggests that the Co layers experience volume expansion of ~ 31.33 % compared to bulk phase, under 20% tension along in-plane.

Each Co layer in the hybrid structure has slightly different a(\text{Co})/a(\text{CoO}) ratio depending on the position and thickness. Co layers have lower a(\text{Co})/a(\text{CoO}) ratios going from the interface to the surface layer. This means that surface Co layers tend to have a slightly denser structure, while interfacial Co layers form a looser structure, relatively. The central region of Co layers (neither surface nor interfacial layer) in Co(4)/CoO(111), exhibits a similar ratio to the middle ideal value, which shows that thicker Co layers have the strained structure of bulk Co in the center. These thickness-dependent structures of Co layers, are expected to cause different interfacial properties as well as different photocatalytic behaviors in the Co(\(x\))/CoO(111) structures, as observed in the examination of other properties [80,220,227-228,231,235-244].
Figure 4.35 (a) Atomic configurations of Co($x$)/CoO(111) hybrid structures constructed with different numbers of Co layer, $x$. Blue and red circles are Co and O atoms, respectively. The number above each figure denotes $x$ in Co($x$)/CoO(111). Each atomic Co layer is named Co-$n$ from the interfacial Co layer (Co-0) to the surface Co layer (Co-$x$) in the Co($x$)/CoO(111). (b) Lattice parameter ratio of Co and CoO layers along thickness axis as defined in the inset. The number in the legend is $x$ in the Co($x$)/CoO(111). The horizontal axis is about two adjacent Co layers, for example, 4-3 denotes two adjacent Co-3 and Co-4 layers as named in Figure (a). The lattice parameter of CoO layer is obtained from the central region of the symmetric supercell. (c) A schematic showing the actual Co structural state between two ideal structural states: 20% tensile strained structure along in-plane with volume conservation and the unstrained structure same as the bulk FCC-Co.

4.4.4 Work function of Co/CoO(111) surfaces

When a metal and a semiconductor are brought into contact, atoms and electrons are redistributed at the interface until the equilibration of the electrochemical potential is achieved. The equilibration process is accompanied by the electron transfer across the interface, which results in the formation of a space charge layer in the semiconductor at the interface. As a result, the conduction and valence band edges at the interface deviate from their bulk values, which in turn bends the energy bands of the semiconductor and forms SBH for charge transfer ($\phi_e$ for electron and $\phi_h$ for hole).

The degree/direction of band bending and the SBH formed at the interface have long been commonly correlated with work functions ($\Phi$) of the two different materials because the amount/direction of electron transfer is characterized by the relative electron affinities of bulk phases of the two materials; a
material of high work function strongly attracts electrons and vice versa. However, the band bending aspects and SBH frequently deviate from the prediction with work functions of bulk phases since the work functions of materials are influenced by the surface state, e.g., surface orientation, adsorbates, roughness and thickness [245-246].

Figure 4-36(a) shows the change in work functions of the Co/CoO(111) hybrid structures with variation of Co layer thickness in the structure. For comparison, work functions of isolated and undeformed Co(111) and CoO(111) slabs (named ‘IU-Co’ and ‘IU-CoO’) with different thickness are shown in Figure 4-36(b). The work function of the entire Co/CoO hybrid structure (blue square in Figure 4-36(a)) decreases up to Co(2)/CoO(111) from the bare CoO(111) slab; it increases again beyond the critical thickness of Co layer. This demonstrates that even though the same materials (Co and CoO in this study) form the heterointerface, the created interface has different electron affinities depending on the Co layer thickness, which deviates from the prediction with work functions of their bulk phases [247]. In addition, work function of Co(111) layers isolated from the hybrid structure (named ‘I-Co’, red triangle in Figure 4-36(a)), also slightly decreases up to 2 atomic Co layers, followed by an increase beyond the critical thickness. The variation in work function of the 1 ─ 2 layered I-Co slabs does not follow the trend of the IU-Co slabs which monotonically increases with increasing the Co thickness. In contrast, the variation of the 2 ─ 4 layered I-Co slabs seems to similarly trace the change in the IU-Co slabs (green diamond in Figure 4-36(b)). This is because the work function of Co slabs is sensitive to strain, the magnitude of which is also dependent on the Co layer thickness (Figure A-6 in the Appendix) Also, a slightly reduced work function in the I-Co slabs than in the IU-Co slabs seems to be related to the tensile strain exerting on the I-Co at the interface, since tensile strain decreases work function of the FCC-Co(111) slabs (Figure A-7 in the Appendix).

A close look at Figure 4-36 provides an interesting point that there is a cross point between the work functions of Co and CoO layers, around 3 or 4 Co layers both in I-Co/I-CoO (Figure 4-36(a)) and in IU-Co/IU-CoO (Figure 4-36(b)). This suggests that the relative electron affinities of Co and CoO layers suddenly become the opposite around the critical Co layer thickness; consequently, the direction of electron transfer becomes the other direction. That is, the variation of Co layer thickness can simply modulate the electronic characteristics of the Co/CoO (111) interface. This modulation is unavailable with the change of CoO layer thickness, because the work function of the IU-CoO slabs scarcely changes with respect to thickness (gray triangle in Figure 4-36(b)). Therefore, changing the work function of the Co layer with thickness, as we do in this study, is suitable to control the interfacial electronic structure of the Co/CoO core-shell structure.
Work functions of (a) Co/CoO(111) hybrid structures as a function of number of Co layers, (b) isolated and undeformed FCC-Co(111) and RS-CoO(111) slabs (IU-Co and IU-CoO) as a function of number of layers. In figure (a), work functions of Co and CoO layers isolated from each hybrid structure are superimposed on the figure (denoted as I-Co and I-CoO). The variation in work functions of IU-Co and IU-CoO is extrapolated by $\Phi_{Co(111)} = 0.118 \times \# \text{ of Co layer} + 4.073$ (green dashed line) and $\Phi_{CoO(111)} = 0.0062 \times \# \text{ of CoO layer} + 4.517$ (gray dashed line) in figure (b). The cross point of green and gray lines in figure (b) is $\sim 3.98$.

**4.4.5 Schottky barrier height at interface**

In this section, to confirm the predicted change in the interfacial electronic characteristics at around 3 – 4 Co layers, we examine SBHs for electron and hole ($\phi_e$ and $\phi_h$), charge transfer at the Co/CoO(111) interface and band bending in the CoO(111) layers. Figure 4-37(b) shows an example of the local density of states (LDOS) of each Co and CoO layer in Co(1)/CoO(111) hybrid structure as denoted in the atomic configuration of the structure (Figure 4-37(a)). The interface of the Co/CoO(111) structure presents metallic behavior, since there is no energy gap in the DOS. The central region of the CoO(111) has a band gap of $\sim 2.6$ eV between the conduction and valence band edges, which is in good agreement with the band gap of bulk RS-structured CoO [42,46,49,50]. $\phi_e$ (or $\phi_h$) is measured from the energy difference between the Fermi level ($E_F$) of the Co/CoO(111) structure and the $E_C$ (or $E_V$), as shown in Figure 4-37(b). The $\phi_e$ (or $\phi_h$) gradually increases (decreases) with increasing the thickness of Co layer. This shows that as Co layer becomes thicker, electron transfer from Co to CoO becomes less probable, while hole transfer becomes easier. Between 3 and 4 Co layers, the sign of $\phi_h$ suddenly becomes the opposite, suggesting no barrier for hole transfer, that is, the formation of Ohmic contact between the Co and CoO layers.
Figure 4-37 Examples of (a) atomic configuration of Co(1)/CoO(111) structure numbering each Co and CoO layer and (b) the local density of states (LDOS) of Co and CoO layers in the Co(1)/CoO(111) structure with respect to $E - E_F$. (c) Schottky barrier heights (SBHs) for electron and hole in Co(x)/CoO(111) hybrid structures with different number of Co layers, $\phi_e$ and $\phi_h$ in Figures (b) and (c) indicate SBHs for electron and hole.

4.4.6 Energy band bending in CoO layer

Since the space charge layer width (10 nm ~ several µm) is larger than the CoO thickness (the size of the Co/CoO(111) core-shell observed in experiment [89] is about 10 nm in diameter), the band bending effect is ignorable in the CoO layer in the Co/CoO core-shell nanoparticles. But, to understand charge transfer behavior between metallic Co and semiconducting CoO layers in the process of electrochemical potential equilibration, we predict the intrinsic band bending occurring in the CoO layers by drawing the $E_C$ and $E_V$ at the interface with respect to those of the bulk CoO phase [103-104], as shown in Figure 4-38. The band bending is downward in the hybrid structures with 1 – 3 Co layers, the degree of which decreases with increasing the Co layer thickness. Yet it suddenly becomes upward in the Co(4)/CoO(111) structure. These thickness-dependent band bending aspects stem from the thickness-dependent electron affinity of the Co layer relative to that of the CoO layers in the hybrid structure: $\Phi_{Co}$ is smaller than $\Phi_{CoO}$ in the hybrid structures with 1–3 Co layers, whereas it is greater in Co than in CoO, in Co(4)/CoO(111) structure, i.e., $\Phi_{Co} > \Phi_{CoO}$, as predicted in Figure 4-36(a). These band bending aspects provide the important information that electrons transfer from Co to CoO in the hybrid structures with 1 – 3 Co layers in the electrochemical
potential equilibrium process, while electrons are collected from CoO to Co in the Co(4)/CoO(111) structure. From the Co(4)/CoO(111) structure (for a thick enough Co layer) to the thicker Co layer decorated hybrid structure (more than 4 atomic Co layers), upward band bending occurs as expected from work functions of bulk Co and CoO phases: Co attracts electrons more strongly than CoO, electrons are depleted in the CoO layer near the interface, resulting in upward band bending.

The different band bending aspects lead to the different charge state of the Co/CoO surface. The larger downward band bending in the CoO layer means more electrons come to the CoO layer from Co layer, because of the intrinsically more $p$-type semiconducting nature of the CoO layer. Accordingly, less electrons are anticipated to transfer to the CoO layer as the Co layers are thicker; consequently, more electrons are present in Co layers. In particular, in Co(4)/CoO(111) structure, electrons are collected to the Co layer from CoO, thus, the surface Co layer become the most negatively charged.

![Band bending in Co(x)/CoO(111) hybrid structures](image)

**Figure 4-38** Band bending in Co(x)/CoO(111) hybrid structures with respect to bulk CoO, with different Co layer thickness, $x$. The number at the top of each graph denotes $x$ in the Co(x)/CoO(111) structures. The conduction and valence band edges ($E_C$ and $E_V$) of bulk CoO are determined by the experimentally observed value; the fermi level is $\sim 0.3$ eV above the $E_V$ [103-104]. The horizontal gray dashed line denotes the $E_F$ of each Co/CoO(111) structure, the width of the space charge layer in the CoO was arbitrarily determined.

### 4.4.7 Charge state of Co layer

To demonstrate our explanation of the relative charge state in the previous paragraph, we investigate the LDOSs of Co layers in the hybrid structures (blue line in Figure 4-39). To understand the intrinsic energy state of each Co layer without the hybridization with CoO, we consider the LDOSs of the
Co layers isolated from the Co/CoO(111) hybrid structure (I-Co, red line in Figure 4-39). The LDOSs of Co layers in the Co/CoO(111) structures with 1─3 Co layers (blue line) locate in higher energy than the I-Co layers. This suggests that the occupation of electrons in the Co layer decreases as a result of electron movement to the adjacent CoO layer as expected from the downward band bending aspect of CoO layer (Figure 4-38). The decline in the electron occupation is more severe at the surface Co layer than at the interfacial Co layer, which directly shows that less electrons exist at the surface Co layers because of electron transfer to the CoO layers. In contrast, the LDOSs of Co layers in the Co(4)/CoO(111) structure shift to lower energy compared to the I-Co, suggesting that electrons come to Co layer and fill the energy state of the Co layer. The degree of the shift to a lower level is greater in the surface Co layer than in the interfacial Co layer. This shows that more electrons are gathered in the surface layer, which results in the negatively charged Co surface. In summary, the surface Co layers are more negatively charged with increasing the Co layer thickness in the Co/CoO hybrid structures.
Figure 4-39 Local density of states (LDOSs) of Co layers in Co\(x\)/CoO(111) structures (blue lines) and of Co layers isolated from the Co/CoO(111) structures (I-Co, red lines). The vertical axis of each graph is \(E-E_F\) (eV). Numbers in the vertical axis denote the number of Co layers \((x)\) in the Co\(x\)/CoO(111) structures, numbers in the top horizontal axis denote the position of Co layer in each structure as noted in the inset.

4.4.8 HER by light absorption of CoO

In sections 4.4.7 and 4.4.8, to understand how the different characteristics of Co/CoO hybrid structures affect the hydrogen evolving ability of the hybrid structure, we examine two kinds of photocatalytic behavior, \textit{i.e.}, SPR effect in Co layer and light absorption in CoO layer, independently, with variation of Co layer thickness. Based on the examination, we predict an optimal thickness of Co layer for the active creation of hydrogen on the Co/CoO(111) photocatalysts from water splitting.
4.4.8.1 $E_C$ vs. $H^+/H_2$

Conduction and valence band edge positions of a semiconducting material relative to water redox potential is a critical criterion measuring whether light absorbed by the semiconducting photocatalyst can trigger HER and OER as suggested in Section 4.2. This criterion is based on the idea that HER (OER) occurs only when electrons (holes) generated by light absorption have enough energy to overcome the kinetic barriers for the HER (OER), i.e., $E_C$ more negative than $H^+/H_2$ or $E_V$ more positive than $H_2/O_2$ (vs. NHE). To evaluate the energy state of the photogenerated electrons in an aqueous solution, we predict the $E_C$ vs. $H^+/H_2$ of the CoO layer in each Co($x$)/CoO(111) hybrid structure with an explicit solvation method as introduced in Ref. 60 and Figure 4-40. Figure 4-40(a) shows an example of the supercell of water/Co/CoO(111) constructed in this study for the calculation of potential drop at the interface of the Co/CoO(111) hybrid structure and water. The calculated planar averaged Hartree potential of the water/Co(2)/CoO(111) structure is plotted as a function of position in Figure 4-40(b).

**Figure 4-40(a)** Snapshot of the atomic distribution of the water/Co(2)/CoO(111) interface. Blue, red, and white circles indicate Co, O, and H atoms, respectively. **(b)** Planar-averaged Hartree potential of the water/Co(2)/CoO(111) interface computed for the structure shown in (a). Dotted red line in (b) indicates macro-averaged Hartree potentials obtained using the approach in Ref. 98.
As shown in Figure 4-41, with decoration of one atomic Co layer, the $E_C$ of CoO layer is more negative than that of the bare CoO(111) surface by $\sim 0.4\,\text{V}$, while it shifts to positive potential with further increasing the Co layer thickness. Since the $E_C$ of the CoO layer is located above the $\text{H}^+/\text{H}_2$ level in the Co(1)/CoO(111) and Co(2)/CoO(111) structures, it is anticipated that the formation of a metallic Co layer on CoO(111) improves photocatalytic HER activity compared to the bare CoO(111), with electron energy higher than the $\text{H}^+/\text{H}_2$ level. However, further increase of the Co layer thickness beyond the two atomic Co layers, results in a loss of a photocatalytic activity for the HER.

The variation of the $E_C$ vs. $\text{H}^+/\text{H}_2$ with respect to Co layer thickness is relevant to the charge state of the Co/CoO(111) surface. The Co(1)/CoO(111) structure contains many electrons in CoO layers in the process of electrochemical equilibrium of Co and CoO layers as explained in Section 4.4.4 (Figures 4-39 and A-8 in the Appendix). Therefore, when the Co(1)/CoO(111) structure is positioned in an aqueous environment, less electrons transfer from water to CoO layer, which results in the more negative $E_C$ vs. $\text{H}^+/\text{H}_2$. However, in Co(4)/CoO(111) hybrid structure, electrons move to the Co layer from the CoO layer in the process of the electrochemical equilibrium of the two materials (Figure 4-38), and the CoO layer becomes comparatively positively charged. Therefore, the CoO layer in the Co(4)/CoO(111) structure accepts more electrons from water at the moment of immersion in water, exhibiting more positive $E_C$ vs. $\text{H}^+/\text{H}_2$ (Section 4.1).

![Figure 4-41 Conduction band edge ($E_C$) positions relative to water reduction potential ($\text{H}^+/\text{H}_2$) of CoO(111) layers in Co($x$)/CoO(111) hybrid structures in pH = 1.](image)
4.4.8.2 Charge separation in Co/CoO structure

In general, in the metal/semiconductor heterojunction systems, the photogenerated electrons are normally separated to the metal, and work for HER on the metal with reduced HER overpotential. Therefore, the metal serves as HER co-catalyst on the semiconductor. In the Co/CoO(111) hybrid structures, considering that the energy band bends downward in the CoO layers in the Co/CoO(111) structure with 1 – 3 Co layers (Figure 4-38), it is energetically likely that photogenerated electrons move to Co layer, and holes remain in CoO layer. Moreover, hydrogen is much easier to be evolved on the Co(111) surface rather than on the CoO(111) surface, with reduced HER overpotential (Figure A-9 in the Appendix). Hence, HER is expected to actively occur on the Co layer rather than on the CoO layer in which charged carriers are generated by light absorption.

4.4.8.3 HER overpotential on Co/CoO surfaces

However, we still do not know whether the photocatalytic HER occurs on the Co(1)/CoO(111) or the Co(2)/CoO(111) hybrid structure, only with band edge positions of light absorbers (CoO in this study). This is because whether the energy of the photogenerated electrons is high enough to overcome the kinetic barriers for HER on the Co/CoO layer is unknown, without understanding the transition state of the HER on the Co/CoO layer. Therefore, we calculate the HER overpotential ($\eta^{HER}$) which indirectly informs the energy state of the transition state of the HER, that is, the energy barrier. The HER overpotential of a surface has been widely calculated using free energy change for hydrogen adsorption, $\Delta G_{H^*}$. As the energy change of a surface is closer to 0 ($|\Delta G_{H^*}|$ is smaller), HER overpotential of the surface becomes lower, resulting in higher HER activity on the surface.

The very low HER overpotentials observed in the Co(1)/CoO(111) and Co(2)/CoO(111) structures (Figure 4-42) are also consistent with the experimentally measured HER overpotential comparable to the commercial Pt/C catalyst [89,248]. The low HER overpotential is possible because hydrogen adsorption-desorption readily occurs on the thin Co decorated hybrid structure, with ignorable electron exchange between the adsorbed hydrogen and the Co/CoO surface (Figure A-10 in the Appendix). Due to the negligible electron exchange, hydrogen binds on the Co/CoO surface strongly enough to stabilize the adsorption as well as weakly enough to easily desorb from the surface, which directly causes the most efficient HER (requiring less energy to generate $H_2$). The high HER activity of the Co(1)/CoO(111) is also confirmed with our *Ab-initio* MD study: the Co/CoO(111) in contact with liquid water at 298 K, spontaneously dissociates water molecules to $H^*$ and $OH^*$, and then creates $H_2$ (Figure A-11-1 in the Appendix), while pure RS-CoO(111) and FCC-Co(111) are unable to form $H_2$ (Figure A-11-2 in the
Appendix). The different behaviors between the Co/CoO and CoO surfaces in an aqueous environment seem to come from the very different $\Delta G_{H^*}$ (Figure 4-42): well-balanced adsorption-desorption of H on the Co/CoO(111) surface, while too strong binding of H on the CoO(111).

**Figure 4-42** Free energy change for hydrogen adsorption ($\Delta G_{H^*}$) on Co($x$)/CoO(111) hybrid structures as a function of number of Co layers ($x$) in the structure. All calculations are done with 1/4 H coverage. $\Delta G_{H^*}$ is also computed for pure FCC-Co(111) of 10 layers and shown in figure(b) with ‘FCC-Co’.

### 4.4.8.4 Determination of HER feasibility under irradiation

Both theoretical HER overpotentials estimated from the $E_C$ vs. $\text{H}^*/\text{H}_2$ (Figure 4-41) and the electrochemical HER overpotential estimated with the $\Delta G_{H^*}$ (Figure 4-42), predict that the most active structure for HER is either Co(1)/CoO(111) or Co(2)/CoO(111) structure. In order to determine which surface structure is indeed able to catalyze the HER under illumination without external bias, we use a criterion determining the feasibility of the HER as suggested in Section 4.2: HER occurs when the $E_C$ is more negative than $\eta^{HER}$. That is, only when the photogenerated electrons have enough energy to overcome the kinetic barrier for the HER, can HER occur through the optimal light absorption of the CoO layer without external bias. The predicted HER feasibility, the $E_C$ and $\eta^{HER}$ values used for the determination are summarized in Table 4-6. According to the criterion, two structures, Co(1)/CoO(111) and Co(2)/CoO(111), can dissociate water by light absorption, and spontaneously create H$_2$. However, the pure CoO(111) and hybrid structures with thicker Co layer decoration (beyond the 2 atomic Co layers) are unable to create
hydrogen because the photogenerated electrons do not have energy enough to overcome the kinetic barrier for the HER, originated from the strong H binding to the surfaces.

**Table 4-6** Conduction band edges ($E_C$), overpotential for HER (\(\eta^{HER}\)), and feasibility of HER (f(HER)) of Co\((x)\)/CoO(111) hybrid structures. Feasible reaction is denoted by ‘O’, unfeasible reaction by ‘X’. The unit of $E_C$ and $\eta^{HER}$ is V (vs. NHE).

<table>
<thead>
<tr>
<th>Number of Co layer, (x) in Co((x))/CoO(111)</th>
<th>$E_C$</th>
<th>$\eta^{HER}$</th>
<th>f(HER)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (pure CoO)</td>
<td>0.048</td>
<td>-1.406</td>
<td>X</td>
</tr>
<tr>
<td>1</td>
<td>-0.340</td>
<td>-0.044</td>
<td>O</td>
</tr>
<tr>
<td>2</td>
<td>0.006</td>
<td>0.012</td>
<td>O</td>
</tr>
<tr>
<td>3</td>
<td>0.284</td>
<td>-0.163</td>
<td>X</td>
</tr>
<tr>
<td>4</td>
<td>0.296</td>
<td>-0.428</td>
<td>X</td>
</tr>
</tbody>
</table>

**4.4.9 SPR effect in Co layer**

In addition to the light absorption by the semiconducting CoO layer, the SPR effect is expected in the Co layer when the Co/CoO(111) hybrid structures are exposed to light. The presence of a surface in metals can make ‘plasmons’ which are collective oscillations of free electrons [249-250]. The surface plasmons cause the displacements of the electron gas with respect to their equilibrium position around positively charged ions. The localized surface plasmons (LSP) in metal nanoparticles can be excited by irradiation at a specific frequency [249,251], resulting in the generation of hot carriers. Under the assumption that the Co layers (~ nm thick) decorated on the CoO(111) layer have the surface plasmon resonance frequency of visible light spectrum (similar to that of the 20% stretched thin Co(111) slabs along the in-plane direction [219], we focus on the energy-population distribution of hot electrons in the Co layers in this study.

**4.4.9.1 Energy-population distribution of hot electrons**

The energy distribution of the hot carriers immediately after photon absorption, is determined by the initial states of electrons in the Fermi gas and the incident photon energy ($E_{ph}$). We estimated the energy-population distribution of the hot electrons created in Co layers, with the transition probability ($P(E)$ in Equation 4.6 which describes the joint density of states multiplied by their respective Fermi distribution functions, $f(E)$) as introduced in Ref. 252.
\[ P(E) \propto D(E - E_{ph})f(E - E_{ph})D(E)(1 - f(E)). \] (4.6)

where \( D(E) \) is the electron density of states (DOS) as a function of the electron energy, \( E \). Upon photon excitation with \( E_{ph} \), an electron in the Fermi gas is promoted from \( E - E_{ph} \) to a higher energy state, \( E \). The model of the transition probability in Equation 4.6 was validated for the energy distributions of hot electron/hole in a variety of materials including pure metals, alloys and nanostructures [252].

For the prediction of hot electron energy-probability distribution in the ferromagnetic (FM) Co layer, it is assumed that spin flipping is available at the moment of the transition when the incident light is resonated with the Co layer. The spin flip effect is ignorable in the creation of high energy hot electrons: The hot electron distribution aspect in the energy-population plot was not significantly different from the spin-flip unconsidered [219].

### 4.4.9.2 Energy-population distribution of hot electrons in Co/CoO structure

The energy-population distribution of hot carriers resulted from the decay of the surface plasmons, is the most critical factor that determines how many hot carriers can overcome the SBH at the interface of metal/semiconductor and induce the HER and OER in the system [253-255]. For the prediction of the distribution, we use Equation 4.6. Figure 4-43 shows the predicted hot electron energy distribution in the Co layers in the Co/CoO hybrid structures under 2 eV (\( E_{ph} < E_g^{CoO} \) in Figure 4-43(a)) and 2.6 eV (\( E_{ph} \geq E_g^{CoO} \) in Figure 4-43(b)) photon energies. The reason for the selection of \( E_{ph} = 2 \) and 2.6 eV, is to understand both when the CoO layer can absorb visible light and not. Each Co layer has slightly different energy-population distribution aspect because of the different LDOSs of the Co layers on the CoO core. Owing to the higher photon energy, more hot electrons are populated under \( E_{ph} = 2.6 \) eV than under \( E_{ph} = 2 \) eV. Among the four hybrid structures, the Co(4)/CoO(111) shows the highest hot electron population under both incident photon energies. This makes sense because more energy states are present around the \( E_F \) for electron excitation (Figure 4-39), especially in the Co layers close to the interface (Co-0 and Co-1). Accordingly, more plasmons can excite from the occupied states to the unoccupied states, and create a high population of hot electrons.
Figure 4-43 Energy-probability of hot electron in each Co layer in Co(x)/CoO(111) under the incident photon energy of (a) 2 eV and (b) 2.6 eV. Numbers at the top of the graph denote the number of Co layers in the Co(x)/CoO(111) structures. The black dotted lines are the surface Co layer and the red solid lines are the interfacial Co layer among Co layers. \( \phi_e \) (vertical gray dotted line) is the SBH for electron in each hybrid structure. Hot electrons overcoming the SBH from the interfacial Co layer (Co-0) to the CoO layers is filled with red color for example.

To quantify how many hot electrons generated in the Co layer can overcome the SBH \((E \geq \text{SBH})\) and go over the adjacent CoO layer, we integrate the area of \(E \geq \text{SBH}\) in Figures 4-44(a) and (b) and the results are plotted in Figures 4-45(a-1) and (b-1). Except for the Co(4)/CoO(111) in which hot electrons cannot move to the CoO layer due to the SBH higher than the energy hot electrons have, the numbers of hot electrons overcoming their SBHs are similar in the three Co/CoO(111) structures with 1 ─ 3 Co layers. Under the higher photon energy (2.6 eV in Figure 4-44(b-1)), more hot electrons can transfer to the CoO layer over the SBH than under the lower photon energy (2 eV), since more hot electrons of high energy are populated under the higher photon energy.

However, since the HER occurs more easily in terms of energy on the Co layer (Figure A-9 in the Appendix), hot electrons staying in the Co layer (not overcoming the SBH) are more helpful for hydrogen evolution with the SPR effect. Therefore, we investigate the hot electron population staying in the Co layers in the Co/CoO(111) hybrid structure by integrating the area of the hot electron energy distribution below the SBH \((E < \text{SBH})\) under 2 and 2.6 eV photon energies. The results are shown in Figures 4-45(a-2) and (b-2). The population of hot electrons staying in the Co layer shows no big difference among the Co/CoO(111) structures with 1 ─ 3 Co layers, but a slight increase with the higher photon energy. Since
some hot electrons (holes) overcome the SBH or some are left in the Co layers, hot electrons and holes existing in the confined space (like Co/CoO nanoparticles), are likely to recombine, resulting in the reduced efficiency of the SPR effect.

On the other hand, the Co layers in the Co(4)/CoO(111) structure have enormous hot electrons, especially in the Co-0 and Co-1 layers. These hot electrons in the thick Co layer face the very high SBH ($\phi_e$); therefore, all the hot electrons stay in the Co layers. Furthermore, hot holes have a negative SBH ($\phi_h$), and all hot holes transfer to the CoO layer without any barrier. Since HER energetically prefers to occur on the Co(111) surface (Figures A-9 in the Appendix), whereas OER prefers to happen on the half hydroxylated CoO(111) surface (Section 4.2), the efficient separation of hot electrons and holes minimizes their recombination rate, and accordingly, maximizes the photocatalytic efficiency for HER or OER with the SPR effect.

(a) $E_{ph} = 2$ eV

(b) $E_{ph} = 2.6$ eV
Figure 4-44 Population of hot electrons (denoted as Area in vertical axis) 1) overcoming SBH for electron with $E \geq SBH$, 2) staying in Co layers not going over the adjacent CoO layers with $E(TS) < E < SBH$ under illumination of (a) $E_{ph} = 2$ eV and (b) $E_{ph} = 2.6$ eV. The number in the legend denotes the number of Co layer ($x$) in the Co($x$)/CoO(111) hybrid structures. $E$ is the energy of hot electrons, $E(TS)$ is the energy required for triggering HER, which is determined by the calculated HER overpotential, $\Delta G_{H^+}$. All hot electrons generated in Co layers of Co/CoO(111) structures have higher energy ($E$) than the energy of transition state of the HER (Figure A-12 in the Appendix), thus, the hot electrons generated in Co layers can trigger the HER without further application of external energy.

4.4.10 Summary and optimal Co layer thickness for active HER

This study identifies the interfacial characteristics of the Co/CoO(111) core-shell structures formed in a reducing environment. The created Co(111) layers are subjected to 20 % tensile strain along the in-plane direction, forming the epitaxial structure with the underlying CoO(111) core. The structural state of the Co layers is close to the structure under the tensile deformation with Poisson’s ratio of Co. The interfaces formed in the Co/CoO hybrid structures with different Co layer thickness have different magnitude of SBH for electron and hole transfers and band bending aspects: 1) SBH for electrons (for holes) increases (decreases) as the Co layer thickness increases, 2) the degree of downward band bending of the CoO layer at the interface decreases, and it suddenly becomes reverse direction (upward band bending) over the critical Co thickness. This variation is closely related to the change in the relative electron affinities of the Co and CoO layers according to the change of work functions of the Co and CoO layers in the hybrid structures. The Co layer thickness-dependent interfacial characteristics determined by the electron transfer across the interface, eventually, determine the comparative charge states of the Co layer and Co/CoO interface, making the Co layer (CoO layer) more negatively (positively) charged. The different charge states of the Co surface and Co/CoO interface also vary the photocatalytic behaviors of the Co($x$)/CoO(111) hybrid structures, i.e., both SPR effect in Co layer and light absorption by the CoO layer for HER.

The comparative photocatalytic properties of the Co/CoO(111) hybrid structures predicted in this study, are summarized in Table 4-7. Under illumination of $E_{ph} < E_{g}^{CoO}$, only SPR effect in the Co layer is expected since the CoO layer cannot absorb light. The SPR effect is high in the thick Co layer decorated structure (Co(4)/CoO(111)); therefore, hydrogen is expected to actively evolve on the hybrid structure from water splitting. Under illumination of $E_{ph} \geq E_{g}^{CoO}$, the SPR effect is still high in the thick Co layer deposited structure for $H_2$ evolution, but, the effect is more pronounced than under smaller $E_{ph}$. Another effect, HER by the light absorption by the CoO layer, practically occurs only on the thin Co layer decorated hybrid structures such as Co(1)/CoO(111) or Co(2)/CoO(111), because light absorbed by the CoO layers has enough energy to induce the HER on the Co/CoO(111) surfaces. In short, for $H_2$ evolution from water
splitting by the SPR effect, a thick Co layer is needed to be deposited on the CoO(111) layer, yet, a thin Co layer is required for the optimal band edge and low HER overpotential to induce the HER on the hybrid structures under irradiation.

**Table 4-7** Summary of photocatalytic properties of Co(x)/CoO(111) (x is the number of Co layer) under photon energy smaller than the band gap of CoO ($E_{ph} < E_g$), and larger than the band gap of CoO ($E_{ph} \geq E_g$). Two photocatalytic behaviors, plasmonic properties (denoted ‘SPR effect’) and light absorption by CoO layer (denoted ‘Light absorption’), are considered. A feasible reaction by the light absorption of CoO layers denotes ‘O’, infeasible one ‘X’. The SPR effect is compared arbitrarily ‘low’ or ‘high’ based on Figure 4-44.

<table>
<thead>
<tr>
<th>Co layer thickness, x in Co(x)/CoO(111)</th>
<th>$E_{ph} &lt; E_g$</th>
<th>$E_{ph} \geq E_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SPR effect</td>
<td>Light absorption</td>
</tr>
<tr>
<td>0</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>1</td>
<td>Low</td>
<td>X</td>
</tr>
<tr>
<td>2</td>
<td>Low</td>
<td>X</td>
</tr>
<tr>
<td>3</td>
<td>Low</td>
<td>X</td>
</tr>
<tr>
<td>4</td>
<td>High</td>
<td>X</td>
</tr>
</tbody>
</table>
CHAPTER 5. CONCLUSION

5.1 Summary of overall water splitting

This study first suggests how overall water splitting can occur on a self-standing CoO nanoparticle photocatalyst with high photocatalytic efficiency and without a co-catalyst or an external bias, using DFT calculations. We predicted that thermodynamically stable morphology of CoO nanoparticles in an aqueous environment is a truncated octahedron with dominant facets of OH*-CoO(111) and CoO(100). Of the two facets, the OH*-CoO(111) facet has the optimal band edge positions for overall water splitting, which explains the reason for the upshift of band edge positions in CoO nanoparticles (more negative $E_C$ and $E_V$ vs. NHE) compared to CoO micropowders (or bulk CoO). However, the CoO(100) facet exhibits more positive $E_C$ and $E_V$ vs. NHE due to positively charged surface characteristics, different from the negatively charged OH*-CoO(111) facet. The very different band edge positions of the CoO(100) and the OH*-CoO(111) facets, form large built-in potential in the CoO nanoparticles, resulting in the efficient charge separation even without an external driving potential, such that electrons are driven to the CoO(100) facet while holes are to the OH*-CoO(111) facet. This is suggested to be the origin of the high photocatalytic efficiency observed experimentally during the photocatalytic overall water splitting on the CoO nanoparticles. Also, it is demonstrated that the separated electrons can trigger HER on the CoO(100) facet, holes OER on the OH*-CoO(111) facet, under the photo-given potential. This clarifies the reason for the spontaneous evolutions of H$_2$ and O$_2$ on the CoO nanoparticles without an external bias or a co-catalyst.

Our thorough understanding of the overall photocatalytic water splitting mechanism for all three steps of photocatalysis (generation of charge carriers under illumination, separation of the photoexcited carriers, and the surface H$_2$ and O$_2$ evolution reactions) provides insight into the photocatalytic mechanism on a variety of single material photocatalysts, on atomic scale.

5.2 Main achievements

1) We proposed new criteria for determining the feasibility of each half reaction on a surface, based on the idea that the energy levels of the photogenerated charged carriers are higher than that of the transition state so that the charge carriers can trigger the half reactions without external driving potential, but with only photon energy absorbed by the surface; $E_C \leq \eta^{HER}$ for HER and $E_V \geq \eta^{OER}$ for OER. This can be screening criteria for evaluating the HER and OER activities of various materials and surfaces.
2) This study, for the first time, revealed the big discrepancy in the $E_C$ and $E_V$ of TMOs experimentally measured in vacuum and in an aqueous solution, contrary to the general belief that the $E_C$ and $E_V$ of materials measured in vacuum are the same as those in an aqueous solution.

3) We demonstrated that general DFT calculations of slabs with a vacuum layer cannot predict the photocatalytic capability for water splitting. Therefore, inclusion of explicit water molecules in DFT calculations is essential for understanding the band alignment of a material to water redox level in a real operating environment and for accurately modeling the surface band edge positions measured from flat band potential in an aqueous environment. We successfully predicted the band edge positions of an antiferromagnetic material in direct contact with liquid water, which are in good agreement with the experimental measurements.

4) We elucidated that water causes a strong delocalization of the electrons in the $d$-bands of the cobalt atoms (weakening of on-site Coulomb repulsion, i.e., $e-e$ interaction) in CoO surface, which results in the loss of magnetic moment of the cobalt atoms. Therefore, we suggested that for an explicit solvation method, spin polarization and $U_{\text{eff}}$ correction are no longer needed for the best fit to the experimental measurements. Based on the optimized computation conditions for the explicit solvation calculation of magnetic materials, we extended and validated the conditions to the first row of transition metal oxides (both paramagnetic and magnetic). We strongly believe that our work will be a milestone in the explicit solvation methods for the prediction of the band edge positions.

5) We also investigated the interfacial characteristics of the Co/CoO(111) core-shell structures formed in reducing environment, as a function of the Co layer thickness, and how the created Co layers and interfaces respond to the photons absorbed by the core-shell structures. Based on the study, we predicted the optimal Co layer thickness for active HER from water splitting such that the thin Co layer is needed for $\text{H}_2$ generation by light absorption of the CoO layer, while thick Co layer beyond the critical threshold is required for $\text{H}_2$ evolution with SPR effect in Co layers. This study provides a strategy for designing optimal structures and thickness for efficient solar energy conversion on various hybrid structures, by controlling the interfacial characteristics.
APPENDIX

A.1 Complexity of CoO(111) surface in an aqueous environment

Figures A-1(a) and (b) show atomic configurations of bare CoO(111) and fully hydroxylated CoO(111) (OH*-CoO(111)) surfaces before and after \textit{ab initio} molecular dynamics (AIMD) relaxation in direct contact with water molecules. The bare CoO(111) surface, which is thermodynamically unstable in an aqueous environment (section 4.1), dissociates H$_2$O near the surface into -OH and –H and some of the created –OH and –H are adsorbed on the surface. The coverage of OH and H and the atomic configuration of the adsorption are different from the way adsorbates are usually considered on slabs of interest in DFT calculations. On the other hand, the OH*-CoO(111) surface that is thermodynamically stable in an aqueous environment (Section 4.1) does not react with water, maintains a surface environment close to the initial state except for thermal vibration due to the elevated temperature effect (at 298 K). This implies that the actual surface environment of CoO(111) formed during the photocatalytic water splitting might be more complex than we have thought, even though the final surface environment becomes closer to the fully hydroxylated CoO(111) after equilibration between CoO(111) and water.
Figure A-1 Initial and Ab-initio MD relaxed atomic configurations of (a) bare CoO(111) and (b) OH*-CoO(111) surfaces in direct contact with water molecules, for 100 fs at 298 K. Blue, red, white circles denote Co, O, H. Light Purple and sky blue indicate OH and H which are formed by dissociation of water on the surface.

A.2 OER overpotentials vs. CoO(111) surface configurations

We calculate the HER and OER overpotentials for various surface configurations that can be vastly modified during water splitting. Figure A-2(a) shows free energy change for intermediate state along reaction coordinates (OH*, O*, OOH*, O2). Based on the energy diagram, OER overpotentials of the surface configurations at the equilibrium potential (1.23 V) are evaluated as the highest energy change among the intermediates and plotted with respect to OER scaling parameter, $\Delta G_{O^*}^0 - \Delta G_{OH^*}^0$[70], as shown in Figure A-2(b). We find that the OER overpotentials of CoO(111) vary significantly depending on the surface coverage, and the OER overpotentials form a volcano relation with respect to OER scaling parameter ($\Delta G_{O^*}^0 - \Delta G_{OH^*}^0$), in good agreement with previous studies of other metal oxide catalysts [70]. Most surface configurations of CoO(111) are on the strong-binding leg of the volcano (left side of the summit), while clean CoO(100) surface is on the weak binding leg in the volcano (right side of the summit) which in turn demonstrates again its poor OER activity. It is also interesting to note that the OER activity of the CoO(111) surface is higher in the more OH covered surface (red shaded region) than in less OH covered surface configuration (green shaded region). Ultimately, the most reactive surface configuration for OER is half hydroxylated CoO(111). This implies that OH adsorption assists OER by reducing the kinetic barrier for the reaction up to critical OH coverage (1/2). The surface configurations of the higher OER overpotentials, i.e., OH*(1/2)-CoO(111) and OH*(3/4)-CoO(111) surfaces, especially have stronger OH binding but weaker O binding unlike the other CoO(111) configurations in Figure A-2(a). This tendency is in accordance with the origin of the OER scaling parameter ($\Delta G_{O^*}^0 - \Delta G_{OH^*}^0$) showing a lower O2-evolving overpotential is related to a strong OH and weak O bindings to the surface [70].
Figure A-2 (a) Free energy diagram of CoO(111) surface configurations for oxygen evolution reaction at the equilibrium potential, pH = 0. (b) Volcano plot of OER overpotential with respect to OER scaling parameter, $\Delta G_O^\ast - \Delta G_{OH}^\ast$, based on the free energy changes in Figure (a). OER overpotential of bare CoO(100) surface is marked with a red star in the plot for reference. The notation of surface configurations is the same as the one in Figure 4-21.

A.3 HER overpotentials vs. CoO(111) surface configurations

Figure A-3 shows free energy change for hydrogen adsorption ($\Delta G_H^\ast$) of CoO(111) with various OH, O and H coverage at standard condition (0 V). As can be seen in Figure A-3, the free energy change largely changes depending on the surface configurations from -2.1 $\sim$ 1.65 eV. Considering that the distance of $\Delta G_H^\ast$ from 0 directly indicates HER activity, HER activity alters a lot depending on the surface environment. Among the adsorbates (OH, O, H) on the CoO(111), it is found that OH adsorption makes $\Delta G_H^\ast$ value more negative, and H and O adsorptions have more positive values. Therefore, it is expected that the balanced coverage of the adsorbates can optimize the HER activity of the CoO(111) surface close to 0.
Figure A-3 Free energy change for hydrogen adsorption ($\Delta G_{H^*}$) of CoO(111) with various OH, O and H coverage at standard condition. The notation of surface configurations is the same as the one in the main manuscript. The bottom figure is shown for the comparison of $\Delta G_{H^*}$ change when OH, O, and H are adsorbed on the CoO(111) surface. Blue, red, and green dashed lines (denoted with (1), (2), and (3)) point out the OH, H, O adsorption effect.

A.4 Change of $E_C$ and $E_V$ along HER and OER pathways

Figures A-4(a) and (b) present the change in the $E_C$ and $E_V$ band edge position along OER and HER pathways relative to water redox potential at pH=7. The calculation method is explained in Section 3.4.2.1. For calculations of the change, the OER is assumed to occur on the OH*(1/2)-CoO(111) and HER is on bare CoO(100) since these two surface configurations are expected to induce OER and HER under visible light illumination, as explained in terms of incident photon energy vs. reaction kinetic barrier in the main manuscript. Along both reaction pathways, the band edge positions change little. Therefore, the situation such that the potential drop between two facets (CoO(100) and OH*-CoO(111) in CoO nanoparticle) becomes inverse during the reaction, does not occur. Therefore, the built-in potential in the CoO nanoparticles as well as the charge separation aspect are kept during the overall water splitting reaction, which results in a continuous overall water splitting reaction on the CoO nanoparticles.
Figure A-4 Variations of conduction and valence band edge positions (red and green lines) along (a) OER pathways on OH(1/2)*-CoO(111) and (b) HER pathways on bare CoO(100) at pH=7. The conduction band edge positions relative to water redox potential are calculated with a direct contact of water molecules as explained in Section 4.1. The right side figures of the band edge position show the intermediate states of the OER and HER. The red color characters are adsorbates in each elementary step of the reactions, the dotted line squares are clean surface sites that are uncovered with any adsorbate.

A.5 Mechanical properties of FCC-Co

A.5.1 Defect effect
Figure A-5-1(a) shows stress-strain curves obtained during uniaxial compression and tension of a defect-free supercell of FCC-Co. The perfect supercell exhibits about 9% elastic limit for tension and 11.3% for compression, with yield strength of ~ 23 GPa. However, the elastic limit significantly decreases to ~ 7% for both compression and tension in the supercell containing a stacking-fault (Figure A-5-1(b)). The significant decrease in the elastic limit due to the presence of defect, is interpreted as the reason why the elastic limit in the real experimental measurement is very low (~ 0.2% [234]), unlike the present calculation: the presence of structural defects including stacking-fault, dislocation and void etc., make materials yield at the very lower value of elastic limit as well as the strength compared to the theoretical values. Therefore, the defect-free supercell can have the very high yield strength (in the range of GPa) close to the theoretical strength as observed in Figure A-5-1, contrary to the normal range observed experimentally (in the range of MPa [234]).

In addition, Young’s modulus of Co obtained from the stress-strain curves is about 200 GPa for both the perfect and defect-containing supercell, similar to the experimentally measured value (209 GPa [234]). This means the physical properties related to atomic bond strength are not significantly affected by the presence of the defect. Therefore, in a real experimental measurement, although Young’s modulus does not change much with and without the presence of a defect, elastic limit and yield strength show very lower values compared to the theoretical values.

![Stress-strain curves](image)

*Figure A-5-1* Stress-strain curves of (a) perfect supercell of FCC-Co and (b) a stacking-fault containing supercell of FCC-Co.
Using the MD simulation technique, FCC-Co was modeled by employing the EAM (Embedded Atom Method) potential and using the large-scale atomic/molecular massively parallel simulator (LAMMPS) code [61]. Periodic boundary conditions were applied to the three-dimensional (3-D) directions in order to eliminate the surface effects. FCC-Co supercells were relaxed for 50 ps using NVT ensemble at 10K. Subsequently, uniaxial tensile (or compressive) strain was imposed on the supercells at a rate of $5 \times 10^8$/s at 10K.

<table>
<thead>
<tr>
<th>Aspect ratio (a/c) of a supercell (in Figure A-5-1(a))</th>
<th>FCC-Co w/o defect</th>
<th>FCC-Co w/ defect (in Figure A-5-1(b))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of atoms</td>
<td>900</td>
<td>1000</td>
</tr>
<tr>
<td>Supercell size</td>
<td>$25 \times 22 \times 18.5 , \text{Å}^3$</td>
<td>$25 \times 22 \times 20.5 , \text{Å}^3$</td>
</tr>
</tbody>
</table>

**Cell configuration**

A.5.2 Aspect ratio effect

Figure A-5-2(a) shows stress-strain curves obtained during compressive strain of FCC-Co, with variation of aspect ratio of the Co supercell from 0.3 to 2.1. The MD simulation was performed in the same condition as for Figure A-5-1 except for the varied height of the supercell (with the fixed area of the supercell but different aspect ratio). With decreasing the aspect ratio of the supercell (going closer to thin film structure), the elastic limit increases. This difference is caused by the different stress states subjected to the supercells with different aspect ratio as schematically illustrated in Figure A-5-3.
Figure A-5-2 Stress-strain curves of perfect supercell of Co with variation of aspect ratio (0.3–2.1).

Figure A-5-3 shows the schematics depicting the stress states exerting on the samples with different aspect ratios. Uniaxial stress is decomposed into the normal stress and the maximum shear stress in the plane that is inclined at 45° with respect to the direction of the uniaxial stress. Shear stress is known to play a crucial role in the structural changes of metals. In the case of high aspect ratio close to the general experimental mechanical deformation test condition (Figure A-5-3(a)), the shear stress coming from the uniaxial stress, mainly exerts on the side of height direction. The shear stress over the yield point induces the permanent atomic displacement from the original location by sliding along the shear plane as shown in Figure A-5-4(a). The deformation behavior shown in Figure A-5-4(a) follows the typical plastic deformation of bulk metals.

However, in the structure of low aspect ratio (Figure A-5-3(b)), the shear stresses originated from uniaxial compressive stress acting on the upper and bottom sides of the sample interact with each other, but with opposite direction. Thus, some part of the shear stress can be canceled, and eventually, the actual stress acting on the shear plane can be smaller than the externally applied stress from the uniaxial stress. Therefore, the structure with low aspect ratio (similar to thin film) can sustain more severe external stress and elastic strain compared to the structure with high aspect ratio as observed in Figure A-5-2. Even beyond the yield point (Figure A-5-4 (b)), buckling phenomenon is observed, which suggests that thin film becomes ductile unlike the structure of the high aspect ratio.
**Figure A-5-3** Schematics of stress states exerting on samples with (a) low and (b) high aspect ratio under uniaxial compression. $\sigma_n$ and $\tau_n$ denote normal and shear stresses acting on the shear plane when the plane is subject to the maximum shear strain along 45 degrees of the uniaxial compressive stress ($\sigma_Z$). If uniaxial tension is exerting on the same samples, the direction of the normal stress would be the other direction (pointing out from the shear plane).

**Figure A-5-4** Snapshots of atomic configuration in FCC-Co supercells with aspect ratio, $c/a$ = (a) 2.1 and (b) 0.3, under compressive deformation. The number at the top of each figure denotes the applied engineering strain (%). The vertical red dotted lines are to separate before and after the yielding; the left side of the red line is before yielding, the right side is beyond the yield point.
A.5.3 Size effect

Figure A-5-5 shows the size effect on the elastic limit and yield strength of FCC-Co. As the supercell size decreases (1/5 length of the larger structure), the elastic limit and yield strength increase, even though the two supercells have the same aspect ratio. Since there is no change in the atomic bond strength between Co atoms, Young’s modulus is independent of the supercell size. This means high strength and elasticity close to the theoretical values can be achieved by the size reduction as frequently observed experimentally.

![Stress-strain curves of FCC-Co supercells](image)

**Figure A-5-5** Stress-strain curves of FCC-Co supercells composed of 300 (black line) and 37500 Co atoms (red line) with the same aspect ratio = 0.3.

A.6 Work function change with Co layer thickness under 20% tension

Figure A-6 shows work function of FCC-Co(111) slabs under 20% tensile strain along the in-plane direction (Co-20%, red circle), as a function of Co layer thickness. Along the out-of-plane axis, compressive strain following Poisson’s ratio is applied by changing the lattice distance.

The work functions of the 1—5 atomic layered Co slabs do not show a big difference among them, around 4.1 eV, contrary to the work functions of the undeformed FCC-Co(111) slabs (IU-Co, green square). The pristine FCC-Co(111) slabs show a monotonical decrease of the work function as shown in Figure 4-36. Therefore, although tensile in-plane strain reduces the work function of the FCC-Co(111) slabs, the amount of the decrease is dependent on the slab thickness. The rough tendency shows that the work function largely decreases as the thickness of the FCC-Co(111) slab increases, by the in-plane tensile strain.
Figure A-6 Work functions of pristine FCC-Co(11) slabs (IU-Co, green square) and of FCC-Co(111) slabs under 20% tensile strain along the in-plane direction (Co-20%, red circle), with respect to the Co layer thickness.

A.7 Work function change with strain

Figure A-7 shows the variation of work function of the FCC-Co(111) slab as a function of the in-plane strain. The supercell is composed of 5 atomic layers parallel to the (111) planes, together with vacuum layer of ~ 15 Å. The in-plane strain is applied to the FCC-Co(111) lattice along both x- and y-axis, and the out-of-plane strain perpendicular to the thickness direction (z-axis) is also applied by the strain determined by Poisson’s ratio of Co. As can be seen in Figure A-7, work function of the FCC-Co(111) slab decreases as larger tensile strain is applied along the in-plane direction, while it enhances with increasing the compressive strain.
Figure A-7 Variation in work function of FCC-Co(111) slab with respect to in-plane strain. Negative strain denotes compressive strain, while positive one is tensile strain.

A.8 Schematic of charge state

Figure A-8 shows the relative amount/direction of electron transfer across the interface of Co/CoO(111) structure with different Co layer thickness, which determines the band bending aspects in the CoO layers. As the Co layer becomes thicker (or thinner), electrons move to the Co layer (or CoO layer) in the process of the electrochemical potential equilibration, making the CoO layer more positively charged as schematically illustrated in Figure A-8. Therefore, the degree of upward (or downward) band bending increases (or decreases) with increasing the Co layer thickness. These Co layer thickness-dependent band bending aspects and charge states of the Co/CoO(111) structures are mainly affected by the relative electron affinity of the Co and CoO layers, which are estimated with work functions of the Co and CoO layers.
**Figure A-8** Schematic explaining charge states of CoO layer in Co(x)/CoO(111) hybrid structures, determined by electron transfer process in the electrochemical equilibration process. The process and charge state are explained on band bending diagrams of Co(x)/CoO(111) hybrid structures. The number at the top of each graph denotes $x$ in the Co($x$)/CoO(111) structures. The red arrows in the figures are the direction/amount of electron transfer in the process of electrochemical potential equilibration.

A.9 Choice of core-shell structure for lower HER overpotential

To understand the effect of core-shell structures on HER activity, we classify the Co/CoO core-shell structures into type–I and type–II as shown in Figure A-9. The type–I structure has the Co layer in the shell, and the CoO layer in the core. The type–II structure has the Co layer in the core, and the CoO layer in the shell. Figure A-9 shows the free energy change for hydrogen adsorption ($\Delta G_{H^+}$) of the two kinds of Co/CoO(111) core-shell structures, calculated with DFT. The Co/CoO(111) core-shell structures have different Co layer fractions. Most of the Co/CoO structures have negative $\Delta G_{H^+}$ value, which means hydrogen strongly binds with the Co/CoO structures. As a function of the Co layer fraction in the structures, the $\Delta G_{H^+}$ value shows parabolic change both in type–I and –II, which shows the minimum HER overpotential in the middle of the Co layer fraction. This indicates that there is an optimal Co layer fraction for efficient hydrogen evolution. Between the type–I and type–II structures, the type–I structure has lower HER overpotential than the type–II structure independent of the Co layer fraction as can be seen in Figure A-9. Hence, hydrogen evolution is expected to be easier on the type–I structure than on the type–II structure, and predominantly occurs on the type–I structure.
A.10 Electron exchange between H and Co/CoO and binding strength

To quantify the electron exchange between the Co/CoO surfaces and the adsorbed hydrogen, and the relationship between the electron exchange and the $\Delta G_{\text{H}^\ast}$ (or HER overpotential), we investigate the local density of states (LDOSs) of the outermost surface Co layers both in the Co(x)/CoO(111) structures (blue lines) and in the H-adsorbed Co/CoO(111) structures (orange lines), as shown in Figure A-10. The reason for the selection of only the outermost surface is based on the idea that if there is an electron exchange between the surface and hydrogen in the process of adsorption, the exchange actively occurs on the outermost surface, that is, the surface Co layer.

The LDOSs of the Co layers in the Co(1)/CoO(111) and Co(2)/CoO(111) structures show no big difference between the LDOSs of the bare and the H-adsorbed Co/CoO(111) structures, suggesting that the two structures rarely exchange electrons with H, once H is adsorbed on the surfaces. With the ignorable electron exchange, hydrogen adsorption-desorption readily occurs on the thin Co decorated hybrid structure, therefore, the very low HER overpotentials observed in Co(1)/CoO(111) and Co(2)/CoO(111) structures (Figure 4-41) are possible. We think the state with the very low $\Delta G_{\text{H}^\ast}$ value is the well-balanced bonding state for efficient hydrogen evolution on the Co/CoO(111) surfaces.

On the other hand, the Co(3)/CoO(111) structure shifts LDOS of Co layer to lower energy with hydrogen adsorption, which means electrons occupy more energy states in Co after the adsorption. This
implies that hydrogen binds with Co(3)/CoO(111) more strongly with the electron transfer as suggested in Figure 4-41 with larger negative value of $\Delta G_{H^*}$.

![Graph](image)

**Figure A-10** Local density of states (LDOSs) of the outmost surface Co layers in Co(x)/CoO(111) structures (blue lines) and of Co layers in the H-adsorbed Co/CoO(111) structures (orange lines). Numbers at the top of each graph denotes the number of Co layers (x) in the Co(x)/CoO(111) hybrid structures.

**A.11 Ab-initio MD of Co(1)/CoO(111), RS-CoO(111) and FCC-Co(111)**

Figure A-11-1 shows the snapshots of the initial and *Ab-initio* MD relaxed water/Co(1)/CoO(111) structure at 298 K. The Co(1)/CoO(111) surface spontaneously dissociates water into -OH and –H, near the surface. The created OHs are absorbed on the Co(1)/CoO(111) surface, while some Hs are desorbed from the surface, finally forming an H$_2$ molecule. Although bare RS-CoO(111) surface can dissociate water into OH and H (Figure A-11-2(a)), H$_2$ does not form on the CoO(111) surface. Instead, the OH and H are adsorbed on the surface. FCC-Co(111) is unable to cleave the water molecules and water molecules keep their intact state (Figure A-11-2(b)).
Figure A-11-1 Initial and Ab-initio MD relaxed atomic configurations of Co(1)/CoO(111) hybrid structure, in direct contact with water molecules at 298 K. Blue, red, white circles denote Co, O, H. Light Purple and sky blue indicate OH and H which are formed by dissociation of water on the surface. The H-H bond (sky blue) on the upper right side, indicates the formation of H₂.

Figure A-11-2 Initial and Ab-initio MD relaxed atomic configurations of (a) CoO(111) and (b) FCC-Co(111), in direct contact with water molecules at 298 K. Blue, red, white circles denote Co, O, H. Light Purple and sky blue indicate OH and H which are formed by dissociation of water on the surface.
A.12 Transition state of HER vs. energy of hot electrons

To understand whether the created hot electrons in the Co layers have energies high enough to overcome the kinetic barriers for HER and induce the reaction, we compare the Fermi level of the Co\((x)/\text{CoO}(111)\) structure with the transition state of the HER which is directly related to the kinetic barrier, as shown in Figure A-12. The kinetic barrier is estimated from free energy change for hydrogen adsorption \((\Delta G^\ast)\). Since the created hot electrons in metal have energies higher than the Fermi level, if the Fermi level of the Co\((x)/\text{CoO}(111)\) structure is above the kinetic barrier for HER, hydrogen is expected to be created on the Co layers in the Co\((x)/\text{CoO}\) hybrid structure, with the SPR effect.

As can be seen in Figure A-12, the Fermi levels of the Co\((x)/\text{CoO}(111)\) structures are above the transition state of the HER, which suggests that all hot electrons generated in the Co layers in the structures, can induce the HER, and evolve hydrogen on the hybrid structures.

\[\text{Figure A-12} \quad \text{Energy of the Fermi level and transition state of Co}(x)/\text{CoO}(111) \text{ hybrid structures, where } x \text{ is the number of Co layers. The calculated energy of the Fermi level and transition state is plotted in reference to the absolute vacuum level } (E=0).\]
REFERENCES


