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Optimal methodology for explicit solvation prediction of band edges of transition metal oxide photocatalysts

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The conduction and valence band edges (E_C and E_V) of a material relative to the water redox potential levels are critical factors governing photocatalytic water splitting activity. Here we discuss the large discrepancy in the experimentally measured E_C and E_V of various transition metal oxides (TMOs) in vacuum and in an aqueous solution. We speculate that the discrepancy stems from the different degree of electron transfer across the surface due to the different environment at the surface of the TMOs in vacuum and water. Accurately modeling the electronic structure at TMO/water interfaces is a significant challenge, however. Using first-principles density functional theory calculations on rutile titanium dioxide and cobalt monoxide model systems, here we identify the optimal approaches to accurately predict the band edge positions in vacuum and water. We then validate the optimized schemes on other TMOs, demonstrating good agreement with experimental measurements in both vacuum and water.

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Valence and conduction band edge alignments relative to the water redox potential levels are critical properties of photocatalytic materials for water splitting, primarily determining the feasibility of the hydrogen and oxygen evolution reactions (HER and OER, respectively) from water splitting under illumination. HER (OER) is known to occur when the E_C (E_V) is more negative (positive) than the hydrogen evolution potential level, H^+/H_2 (oxygen evolution potential level, H_2O/O_2).

Historically, first-principles density functional theory (DFT) studies have been used to predict the environment-dependent band edge positions of various surfaces by investigating the electronic structure of slabs with surfaces in contact with a vacuum layer. This idea is based on the assumption that the band edge positions of a material stay the same before and after contact with the electrolyte, i.e., that the band edges measured in vacuum can represent those in an operating environment. However, this assumption is not always a good one, as the band edges before and after contact with an electrolyte have been shown to be different in many systems^{1–14}.

Recently, a polarization continuum model (PCM)¹⁵, an 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 show little difference from those calculated in vacuum^{16,17}. Furthermore, they have not correctly predicted the band edges measured from flat band potential in water. We suggest that the implicit solvation calculation method fails to reproduce the experimental band edge alignments in an aqueous solution because the model is unable to describe the electron exchange occurring at the realistic surface/water interface.

Wu et al.¹⁸ pioneered an explicit solvation method to assess the band edge positions at a material/aqueous solution interface, which successfully reproduces values close to experimental measurements for various materials. Cheng et al.¹⁹ and Kharche et al.²⁰ also performed *ab initio* molecular dynamics (MD) simulations with explicit water to explore the band edge positions in an aqueous solution. However, these materials are primarily non-TMOs, and also paramagnetic, and thus do not have complex magnetic configurations and Hubbard U correction parameters (U_{eff}). Understanding the effects of explicit solvation on both paramagnetic and magnetic metal oxides is crucial, however, as many magnetic metal oxides including CoO, Co_3O_4 , FeO, Fe_2O_3 , NiO, MnO and Cr_2O_3 , as well as non-magnetic metal oxides such as TiO_2 , WO_3 , and others, are potential catalysts for photocatalytic OER, HER, and other aqueous chemical reactions. Currently, there is no general approach for determining which materials require explicit solvation at the first-principles level in order to accurately capture their electronic structure and catalytic properties. Furthermore, a systematic understanding of the roles played by spin polarization and U_{eff} on the results of calculations of oxides in explicit solvent have yet to be developed.

In this study, we begin to address these issues by using DFT calculations to investigate the band edge positions of two test materials of interest for photocatalytic water splitting, anti-ferromagnetic CoO and paramagnetic rutile TiO_2 , in vacuum and in contact with explicit water. Based on the results, we demonstrate that the inclusion of explicit water at the DFT level of accuracy is necessary in order to accurately predict the band edges in an aqueous solution, as well as to fundamentally understand the material/water interface. Moreover, we suggest an optimal explicit solvation calculation approach by focusing on the effect of spin polarization and U_{eff} values on the band edges of the CoO and rutile TiO_2 model systems. Finally, we verify this approach by extending to various other oxide materials of interest

for photocatalytic water splitting, including magnetic FeO, NiO, and MnO, as well as non-magnetic anatase TiO_2 , WO_3 , and V_2O_5 . In addition to providing a fundamental understanding of these oxide/water interfaces, we expect that the proposed optimized approach will enable more rapid and accurate prediction of the electronic structure and properties of oxide/water interfaces, as well as guide future investigations of other semiconductor/electrolyte systems.

Results

Experimental E_C and E_V in vacuum and in water. The band edge positions relative to the water redox potential levels are significantly influenced by the material^{1,2,21}, crystal structure^{22,23}, surface characteristics^{16,24–26}, and operating environment of a photocatalyst^{27,28}. In the process of the electrochemical potential equilibration between 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 can be significantly affected by the different surface environments. As a result of the electron transfer process, a depletion layer forms at the surface of the photocatalyst, over which band bending occurs, determining the band edge alignment with the water redox potential levels. The band edge alignments at the surface/medium interface directly influence light absorption, the energies of photogenerated charge carriers, and, eventually, the thermodynamics and kinetics of catalytic reactions at the surfaces. Therefore, in order to properly comprehend the photocatalytic water splitting reactions in an operating environment, it is necessary to understand the aqueous environment-dependent band edge positions of materials, which are different from those in vacuum state as shown in Fig. 1.

Figure 1 shows the experimental E_C and E_V of various transition metal oxides (TMOs) as measured in vacuum with UPS (red lines) and in an aqueous solution with flat band potential measurements (black lines). Even at a glance, there is a large change in the band edge positions measured in vacuum and in an aqueous solution for most of these TMOs. This means the surface

Fig. 1 Experimentally measured band edge positions of TMOs in vacuum and in water. Experimental E_C and E_V relative to H^+/H_2 of CoO, FeO, NiO, MnO, CuO, Cu_2O , Co_3O_4 , Cr_2O_3 , TiO_2 , Ta_2O_5 , WO_3 , V_2O_5 measured with ultraviolet photoelectron spectroscopy (UPS) in vacuum state (red filled and open circles)^{3–7} and measured from flat band potential in an aqueous solution (black filled and open circles)^{1,2,8–14} at pH = 1. ' E_C -vacuum' and ' E_V -vacuum' in legend indicate the E_C and E_V measured in vacuum, and ' E_C -water', ' E_V -water' denote the E_C and E_V measured in an aqueous solution. '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 .

states as well as their band edges in vacuum are no longer the same as the states in contact with electrolyte, suggesting a significant environmental effect on the band edge positions. Furthermore, examination of Fig. 1 shows that the band edge positions in an aqueous solution relative to the positions in vacuum reflect the intrinsic semiconducting nature of the material. Specifically, *n*-type semiconducting (or insulating) materials such as Ta₂O₅, TiO₂, WO₃ and V₂O₅, show an upward shift in the band edges in water compared to those in vacuum, which is in agreement with the upward band bending at *n*-type semiconductor/water interface^{27,29–31}. In contrast, CoO, FeO, NiO, MnO, CuO, Cu₂O, Co₃O₄ and Cr₂O₃, known as *p*-type semiconductors, exhibit a downward shift in water compared to vacuum, as a result of electron transfer in the process of electrochemical potential equilibrium between the semiconductor and water^{30,31}. These two findings in Fig. 1 imply that the band edge positions (energy states) calculated with a vacuum layer are similar to the bulk state without much perturbation from vacuum¹⁷, while the band edges measured in an aqueous solution diverge from the bulk state because of a significant perturbation from water³⁰. 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, we suggest that the solvation effects of water need to be explicitly included in the DFT calculations.

Importance of U_{eff} in band edge prediction. The 3d 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 anti-ferromagnetism. 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^{32,33}, 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^{34,35} in which the electrons localized on the *d*-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_{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.

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, E_F) in the solid and the water. Thus, we examine the E_F (referenced to the absolute vacuum level) with respect to the U_{eff} for TMOs to determine the effect of U_{eff} on the band edge positions in vacuum.

Figure 2a shows the computed E_F relative to vacuum level of TiO₂(110) slabs with various surface oxygen stoichiometries and with different U_{eff} values. The E_F is essentially independent of U_{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_{eff} , but are sensitive to the surface stoichiometry. As shown in Fig. 2b, there is indeed little change in

either E_V or E_C of rutile TiO₂(110) slabs in vacuum as a function of U_{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 decreases 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 TiO₂³⁶.

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^{expt}) to the DFT-calculated E_V (blue triangles in Fig. 2b). Considering that rutile TiO₂ prepared at ambient temperature and atmospheric pressure is known to have O-terminated (110) surfaces^{37,38}, 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 E_C is reasonable for TiO₂ in vacuum because DFT-calculated E_V of TiO₂ is very similar to the E_V obtained from DFT calculations in vacuum¹⁹, GW calculations³⁹, QM/MM embedding technique⁴⁰ as well as the experimental value measured in vacuum with UPS^{41,42}. Therefore, even though DFT calculations fail to precisely predict the E_C (or E_g) unlike GW calculations, DFT calculations seem to provide a reasonable E_V in vacuum conditions. In addition, Fig. 2b–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_{eff} (Supplementary Fig. 1) while the DFT+ U computed value of E_C changes more significantly with U_{eff} , resulting in different E_g (Supplementary Note 1 and Supplementary Fig. 1). The figure also shows that the E_V and E_C of the stoichiometric TiO₂ surface in vacuum are consistent with experimental measurements even when determined from DFT calculations without a Hubbard U correction. Thus, applying U_{eff} is not necessary for accurately predicting E_C of rutile TiO₂ in vacuum.

Rock salt CoO is frequently observed to have a magnetic phase in bulk structure⁴³ and nanoparticles⁴⁴. Also, in most DFT studies of the thermodynamic stability of CoO, the AFM-II phase is more stable than any other magnetic configuration for both bulk and surface structures. However, considering its Néel temperature of 291 K⁴³, we expect that paramagnetic as well as antiferromagnetic phases 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 TiO₂(110) slabs in vacuum (Fig. 2a), the E_F changes with surface chemistry, but for a given surface, neither spin polarization nor the value of U_{eff} leads to significant changes, except for the large fluctuation for CoO(100) (Fig. 3a). Therefore, one might expect that the band edge positions are also similar regardless of the spin polarization and U_{eff} . However, Fig. 3b and c show that the E_V and E_C change significantly with the use of spin polarization + U_{eff} , shifting upward more than 2 eV. This significant change suggests that the effects of spin polarization and U_{eff} on band edge positions in vacuum are in fact very large.

The band edge positions estimated with spin polarization + U_{eff} (Fig. 3c) 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 because the DFT-calculated E_g 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)^{8,9}.

Among the various surfaces in Fig. 3c, the CoO(100) slab exhibits the E_V and E_C similar to those measured experimentally. Based on the experimental and theoretical evidence that the CoO (100) facet thermodynamically tends to exist in high vacuum state

Fig. 2 Fermi levels and band edges of rutile $\text{TiO}_2(110)$ in vacuum. **a** Fermi level (E_F) relative to absolute vacuum ($E = 0$) of O-terminated rutile $\text{TiO}_2(110)$ 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_{eff} (no U , 2.5 and 4 eV). **b–d** E_C and E_V for the different surfaces computed with different values of U_{eff} . In panels 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 E_V . The experimental value of E_C measured for rutile TiO_2 in vacuum⁴ is indicated by the horizontal green line

Fig. 3 Fermi levels and band edges of various CoO surfaces in vacuum. **a** Fermi energy levels (E_F) 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** E_C and E_V computed without spin polarization and without U_{eff} . **c** E_C and E_V computed with the AFM-II phase and $U_{\text{eff}} = 4.1$ eV. In panels b, 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 vacuum⁴ is indicated by the horizontal green line

of $\sim 10^{-10}$ Torr ($\sim 1.315 \times 10^{-13}$ atm, $\Delta\mu_{\text{O}} = \sim 0.5$)¹⁷ in E_C and E_V of CoO were measured via UPS⁴, we suggest that the E_V and E_C of CoO in vacuum come from the CoO(100) surface with an AFM-II phase. Also, considering that CoO tends to be cleaved with an exposed (100) plane⁴⁵, CoO(100) is considered as the most probable surface configuration for CoO.

E_C vs. H^+/H_2 in water. To predict the band edge positions of the CoO and TiO_2 surfaces in an aqueous solution, we use an approach similar to the three-step method introduced in ref. 18, which is shown schematically in supplementary Fig. 2. The approach determines the position of the conduction band edge of a material relative to the water reduction potential level, i.e., $E_C - E(\text{H}^+/\text{H}_2)$, based on the computed energy differences between (1) the conduction band edge and the average Hartree potential of the bulk semiconductor ($E_C^{\text{SC}} - H^{\text{SC}}$); (2) the H^+/H_2 level and the average Hartree potential of bulk liquid water ($A^{\text{H}_2\text{O}} - H^{\text{H}_2\text{O}}$);^{17,18} and (3) the average Hartree potential in the semiconductor and water regions of the semiconductor-water interface ($H^{\text{int, SC}} - H^{\text{int, H}_2\text{O}}$). The values for the first and third steps can potentially be affected by spin polarization and/or U_{eff} values since the materials contain 3d transition metals. In the following subsections, we discuss the details of the calculations for each step for both CoO and TiO_2 .

$E_C - H$ value. Spin polarization and U_{eff} significantly affect the value of the energy difference between the E_C and the average Hartree potential of bulk CoO, $E_C^{\text{CoO}} - H^{\text{CoO}}$, as shown in Fig. 4a, changing by almost 4 eV in going from the case with no spin polarization and no U_{eff} to the case of AFM-II and $U_{\text{eff}} = 6$ eV. This large change could distort the value of E_C vs. H^+/H_2 at the end of the three-step calculation. Nevertheless, if the value of $H^{\text{int, CoO}} - H^{\text{int, H}_2\text{O}}$, the potential drop at the CoO/water interface (the value of third step), also changes by the same amount as $E_C^{\text{CoO}} - H^{\text{CoO}}$, then 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_{eff} value. However, this is not the case for CoO and TiO_2 as discussed in Section ‘Potential drop at the interface’.

As we observed in CoO, the $E_C^{\text{TiO}_2} - H^{\text{TiO}_2}$ increases in bulk rutile TiO_2 , with increasing U_{eff} (Fig. 4b). With increasing U_{eff} from 0 to 12 eV, the $E_C^{\text{TiO}_2} - H^{\text{TiO}_2}$ increases by ~ 0.9 eV. This increase can potentially distort the E_C vs. H^+/H_2 obtained at the end of the three-step calculation.

Potential drop at the interface. Figure 5b shows plots of the average Hartree potential in the CoO(100) slab/water supercell as a function of distance along the z -axis (Fig. 5a), showing the potential drop at the interface (the value of the third step) with

Fig. 4 E_C - H value of bulk CoO and rutile TiO_2 . **a** $E_C^{\text{CoO}} - H^{\text{CoO}}$ value (the first step value in the three-step approach¹⁸) of bulk CoO with and without spin polarization and various U_{eff} values. **b** $E_C^{\text{TiO}_2} - H^{\text{TiO}_2}$ of bulk rutile TiO_2 with respect to U_{eff} . Unit of U_{eff} is eV

Fig. 5 Effects of spin polarization and U_{eff} on potential drop at CoO(100)/water interface. **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 (denoted '(R)') and its macro-averaged (denoted '(A)') Hartree potentials of the CoO(100)/water interface computed for the structure shown in panel **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 + $U_{\text{eff}} = 3$ eV. Dotted lines in panels **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 panels **d** and **e**. In case of high U_{eff} values, the amount of distortion is too large to superimpose in panel **b**. Left of the vertical dotted lines in panels **b-e** is CoO(100) slab, right is water in CoO/water supercells

various conditions of spin polarization and/or U_{eff} values. Only the plot of the Hartree potential computed with no spin polarization + no U_{eff} (Fig. 5c) shows an ideal stair-like Hartree potential change between the CoO surface and water regions along the distance as observed in ref. 18, while the plots with other conditions diverge from the ideal plot, 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. The deviation from the ideal potential change is considered to come from the electric field (or artificial dipole) inside the slab/water supercell generated by the applied spin polarization + U_{eff} , as explained in Supplementary Fig. 3. With the aspect distorted from the ideal plot, it is difficult to calculate the accurate potential drop at the surface/

water interface because two distinct macro-averaged potential levels for CoO slab and water regions are difficult to obtain.

However, as Fig. 5b shows, the distortion from the ideal potential drop plot mainly occurs in the water region, considering that the electrostatic potential largely changes by the spin polarization + U_{eff} in the water rather than in the slab (Supplementary Note 2). The different amount of change is regarded to be from the effect of spin polarization and/or U_{eff} , intentionally applied to the water region (Supplementary Fig. 3c), different from the adjacent CoO slab which needs the spin polarization and U_{eff} correction. Also, a close look at the narrow region of the plots close to the interface (Fig. 5c-e), gives us important information; the magnitude of the macro-averaged

Fig. 6 Effect of U_{eff} on potential drop at rutile $\text{TiO}_2(110)$ /water interface. Planar-averaged (denoted '(R)') and its macro-averaged (denoted '(A)') Hartree potentials of the rutile $\text{TiO}_2(110)$ /water interface with variation of U_{eff} value. Unit of U_{eff} is eV

potential drop at the CoO surface/water interface is similar ($H^{\text{int,CoO}} - H^{\text{int,H}_2\text{O}}$ in Fig. 5c-e) or does not change significantly, even though the plots incline by the spin polarization and/or U_{eff} . This implies that if stair-like Hartree potential-distance plots could be obtained from the calculations with AFM-II and/or U_{eff} values, i.e., without distortion coming from the applied spin polarization + U_{eff} correction, the plots may be similar to the ideal potential drop (Fig. 5c). That means again the ideal potential drop at the slab/water interface can be found without consideration of spin polarization and U_{eff} even for the AFM-II CoO phase. Hence, the E_C vs. H^+/H_2 estimated from the three-step method is expected to be solely affected by the $E_C^{\text{CoO}} - H^{\text{CoO}}$, with the ideal potential drop at the interface (Fig. 5c).

As observed at the CoO(100)/water interface, the $\text{TiO}_2(110)$ /water interface also deviates from the ideal Hartree potential drop plot (obtained with no Hubbard U correction) with the application of U_{eff} as shown in Fig. 6. The deviation is smaller than at the CoO(100)/water interface. As for CoO(100)/water interface, we also expect that the ideal plot of Hartree potential-distance as well as the $H^{\text{int,TiO}_2} - H^{\text{int,H}_2\text{O}}$ value for third step can be calculated without the U_{eff} . Therefore, U_{eff} is not needed to obtain the potential drop at the semiconductor/water interface in the explicit solvation calculations for paramagnetic rutile TiO_2 .

E_C vs. H^+/H_2 . Figure 7 shows E_C vs. H^+/H_2 of bulk CoO and CoO surfaces calculated using the three-step approach with various conditions of spin polarization and/or U_{eff} values, by constraining the potential drop at the interface to the ideal value (Fig. 5c). As can be seen in Fig. 7, 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 Fig. 5), 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^{8,9} and CoO micropowders⁹. In addition, $\text{OH}^*\text{-CoO}(111)$ surface releases E_C vs. H^+/H_2 similar to that of CoO nanoparticles in experiments⁹. As demonstrated in the previous study¹⁷, the presence of the $\text{OH}^*\text{-CoO}(111)$ 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 have been shown experimentally⁴⁶ and theoretically¹⁷ to lose their magnetic moments, it is reasonable to carry out the explicit solvation calculation on the CoO/water interfaces without consideration of spin polarization. The loss of magnetic moment

Fig. 7 E_C vs. H^+/H_2 of bulk and CoO surfaces predicted with various explicit solvation conditions. Conduction band edge position (E_C) relative to the water reduction potential (H^+/H_2) of bulk CoO, Co/CoO(111), $\text{H}^*\text{-CoO}(111)$, CoO(100), $\text{OH}^*\text{-CoO}(111)$ 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) plane⁴⁵. Yellow and orange horizontal lines are the E_C s of CoO nanoparticle⁹ and bulk CoO (or micropowder⁹) obtained with flat band potential measurements at pH = 7. Unit of U in legend is eV

Fig. 8 E_C vs. H^+/H_2 of bulk and $\text{TiO}_2(110)$ surfaces predicted with various explicit solvation conditions. Conduction band edge positions (E_C) relative to the water reduction potential (H^+/H_2) of cleaved bulk rutile TiO_2 and rutile $\text{TiO}_2(110)$ 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_{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 rutile TiO_2 measured from flat band potential in an aqueous solution of pH = 18 is superimposed in the figure (horizontal orange line). Unit of U in legend is eV

of Co atoms in the CoO surface is regarded to stem from the mixed spin states induced by the charge transfer between the CoO surface and water⁴⁷. In addition, even though U_{eff} was applied to the Co atoms in the explicit solvation calculation, the interaction of water with the CoO surface significantly broadens the DOS of the Co 3d orbitals¹⁷. This directly suggests that the 3d orbitals are not entirely localized in contact with water, reducing the d-band

splitting^{17,48}. The electron delocalization occurs because metal t_{2g} levels of Co atom overlap with the p orbitals of the water, enabling strong orbital mixing, according to previous experimental⁴⁹ and DFT⁵⁰ works.

Accordingly, an explicit solvation calculation with no spin polarization +no U_{eff} is sufficient to capture the realistic CoO/water interfacial structure, the charge transfer between the CoO and water, band bending aspect, and the band edge alignment to water redox potentials, as we demonstrated in this study.

Figure 8 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 Fig. 7, we fixed the potential drop at the interface to the ideal value obtained from no U_{eff} calculation. The bulk TiO_2 has the lowest band edge position, while it increases gradually from stoichiometric to half- and full-coverage surface oxygen vacancy $TiO_2(110)$ surfaces in sequence. This makes sense because when a neutral oxygen leaves the lattice, excess electrons remain, 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 becomes more reduced. This trend is in agreement with the change in E_C in vacuum (Fig. 2).

Importantly, the calculation with no Hubbard U correction provides E_C vs. H^+/H_2 of rutile TiO_2 closest to the experimental measurement. Therefore, as with CoO, U_{eff} is not required to evaluate the band edge position of paramagnetic TiO_2 in an aqueous solution.

Table 1 summarizes the values of E_C and E_V relative to the H^+/H_2 level for rutile TiO_2 and CoO model systems calculated with vacuum reference and with the 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.

For both rutile TiO_2 and CoO, the E_C in vacuum can be accurately predicted by adding the experimental band gap to the DFT-computed value of E_V relative to the absolute vacuum level ($E_C = E_V + E_g^{\text{expt}}$) rather than taking the direct DFT result for E_C . This is because the DFT-calculated values of E_V for both TiO_2 and CoO are accurate comparable to experimental values. Since the calculated E_V of rutile TiO_2 (110) barely changes with variation of U_{eff} value (Supplementary Fig. 1), the E_C estimated

from $E_V + E_g^{\text{expt}}$ also does not vary much. Therefore, the Hubbard U correction is unnecessary for the accurate prediction of E_C for rutile TiO_2 , although the Hubbard U correction improves the accuracy of the calculated band gap (Supplementary Fig. 1). However, for CoO, the calculated E_C and E_V of CoO in vacuum exhibit values closest to the experiment only when the DFT calculation is conducted on CoO(100) surface with spin polarization (AFM-II) + U_{eff} (Fig. 3). 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_{eff}). The optimal conditions are different depending on materials.

However, the E_C and E_V of bulk rutile TiO_2 and CoO model systems in an aqueous solution are in best agreement with experimental measurements when compute without a Hubbard U correction and without spin polarization as can be seen in Table 1. This means that the explicit calculation of the surface/water interface without spin polarization and without Hubbard U 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. The high accuracy of the E_C estimated from the three-step approach with the explicit water contact was also observed from other explicit solvation calculations^{19,51}. 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 water¹⁸. 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. The E_C and E_V values predicted with this relationship are closer to the experimental values (regardless of the accuracy of the DFT-computed band gap size), because the main charge transfer is due to fast electron transfer from the polar water molecules to the conduction band of the oxide^{52,53} regardless of band gap and electron affinity⁵³.

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_2O_5 as shown in Fig. 9. In all cases, the calculated E_C s vs. H^+/H_2 are comparatively in good agreement with the experimental measurements, except for the vacuum reference calculation of V_2O_5 and WO_3 (not shown in Fig. 9). We expect this discrepancy stems from the inaccurate DFT-estimated E_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 Hubbard U correction or magnetic ordering, which predicts the accurate E_V with a vacuum layer, DFT calculations can be used to 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 (Supplementary Fig. 4); 3) the explicit solvation calculations without consideration of on-site Coulomb interaction + spin polarization can accurately determine the realistic band edges of TMOs in an aqueous solution.

Table 1 Band edges of model systems calculated in vacuum and in water

	Vacuum		Water (at pH = 7)	
	E_C vs. H^+/H_2	E_V vs. H^+/H_2	E_C vs. H^+/H_2	E_V vs. H^+/H_2
Rutile TiO_2 (exp.)	0.10	3.50 Ref. ⁴	0.25	3.61 Ref. ⁸
Bulk TiO_2 - no U_{eff}	—	—	0.18	3.18
TiO_2 (110) - any U_{eff} values	−0.19	2.81	—	—
CoO (exp.)	−1.70	0.70 Ref. ⁴	1.01–1.5	3.50–4.1 Ref. ⁸
Bulk CoO - no spin	—	—	0.93	3.53
+ no U_{eff}	—	—	—	—
CoO(100) - AFM-II + $U_{\text{eff}} = 4.1$ eV	−1.89	0.71	—	—

The values obtained in the present study are marked with green shade. The unit is V (vs. NHE). The negative E_C value denotes the conduction band edge above H^+/H_2 . The E_C of bulk phase is obtained from the cleaved surface of bulk phase relaxed with DFT, with the same three-step calculation approach introduced in Ref. ¹⁸

Fig. 9 Validation of the optimal parameters for the E_C vs. H^+/H_2 in water. Conduction band edge (E_C) positions of CoO, FeO, NiO, MnO, rutile TiO_2 , anatase TiO_2 , WO_3 , V_2O_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, MnO, WO_3 , V_2O_5 in vacuum are calculated for (001) orientated surface, the band edges of anatase TiO_2 in vacuum are computed for (101) surface, with the conditions optimized for bulk phase that can have accurate experimental band gap and magnetic ordering (Supplementary Fig. 4c, d, f). Structural information used for the calculations of all TMOs in this figure is summarized in Supplementary Table 1, and explained in Supplementary Note 1 and Supplementary Fig. 4

Discussion

In conclusion, this study first argues and reveals the large 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 DFT calculations, we find optimal conditions of spin polarization and/or on-site Coulomb interaction parameter (U_{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_{eff} value, magnetic configuration and surface configuration should be identified. Moreover, E_C in vacuum estimated from the $E_V + E_g^{expt}$ 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 Hubbard U 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 $E_V = E_C - E_g^{expt}$ 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_2O_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 is a potential 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.

Methods

Model systems. TiO_2 is a promising candidate for photocatalysis. As a result of its abundance, photo-stability, and reasonable activity, it is currently almost the only material suitable for industrial photocatalytic water splitting applications⁵⁴. In particular, the relatively high photocatalytic activity of TiO_2 for HER or OER originates from the ~ 3 eV band gap and appropriate alignment of the band edges relative to the water redox potentials^{1,8,10,11}. Furthermore, both the band gap and the band edges of TiO_2 can be modulated by the formation of surface oxygen vacancies^{26,36}, providing opportunities for optimizing the activity.

CoO nanoparticles, which have a band gap of 2.4–2.6 eV, have been reported to evolve stoichiometric hydrogen and oxygen from water splitting under visible light irradiation even without an external driving potential or a co-catalyst in neutral water⁹, even though bulk CoO is inactive for photocatalytic water splitting⁹. The CoO nanoparticles hit the record for the highest solar-to-hydrogen photocatalytic efficiency ($\sim 5\%$) for single-material (*i.e.*, no co-catalysts) nano-particulate photocatalysts. The improvement in the photocatalytic properties of CoO nanoparticles relative to bulk is due to the changes in the band edge positions relative to the water redox potential levels⁹. Previously, we demonstrated that the optimal band edge positions are a result of the thermodynamically stable facets present on the nanoparticles but not in larger-sized micropowders or bulk-like crystals¹⁷.

Bulk structure. Bulk rutile TiO_2 was modeled with DFT and DFT + Hubbard U (DFT + U) using VASP⁵⁵ with projected augmented wave (PAW) pseudopotentials from the VASP database and the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)⁵⁶ to describe the exchange-correlation effects (Supplementary Methods). $U_{eff} = 2.5$ – 12 eV were employed for Ti atoms in the DFT + U calculations. 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 < 0.005 eV $\text{\AA}^{-1}$. However, the DFT-relaxed TiO_2 bulk phase underestimated the experimental band gap (3 eV⁵) even with the correction of U_{eff} (Supplementary Fig. 4a).

Experimentally, bulk CoO crystallizes in the rock salt structure and exhibits type-II antiferromagnetic (AFM-II) spin ordering, in which the magnetic moments of the Co atoms are aligned in parallel within each (111) plane, with antiparallel ordering of adjacent (111) planes⁴³. 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 3d shell of Co with U_{eff} varied between 1 and 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 < 0.005 eV $\text{\AA}^{-1}$. For the AFM-II phase of bulk CoO with $U_{eff} = 4.1$ – 5 eV, we find a band gap of 2.3–2.66 eV and a lattice constant of 4.26–4.264 $\text{\AA}$, in reasonable agreement with the experimental values of 2.4–2.6 eV^{8,9} and 4.262 $\text{\AA}$ ^{57,58}, respectively (Supplementary Fig. 4b and ref. 17).

Surface structures in vacuum. To study the band edge positions of rutile TiO_2 with respect to the absolute vacuum level, we consider symmetric $TiO_2(110)$ (1×2) slabs as shown in Supplementary Fig. 5, as the (110) facets of TiO_2 have been shown to have the lowest surface free energy^{37,59,60}. Since the surface oxygen stoichiometry is sensitive to the sample preparation conditions in experiment³⁶, which results in the variation of the band edge positions of the surfaces, we consider a range of surface oxygen vacancy concentration from 0, to 0.5, and 1 per 1×2 surface unit cell. For the structural relaxations of the slabs, a vacuum layer of ~ 15 $\text{\AA}$ and a $8 \times 2 \times 1$ Monkhorst-Pack k -point mesh are used (see Supplementary Methods).

The band edge positions of CoO surfaces in vacuum are examined with symmetric supercells of various surface configurations verified to be present under different oxidation conditions, as determined in the previous work:¹⁷ metal Co decorated CoO(111) (Co/CoO(111)), fully hydrogenated CoO(111) (H^+ -CoO(111)), clean CoO(100), and fully hydroxylated CoO(111) (OH^+ -CoO(111)), together with bare CoO(111) which is unstable for comparison. The computational details are the same as those described in ref. 17, and the structures of CoO surfaces were shown in the SI of ref. 17.

Band edges in explicit liquid water. To predict the conduction band edge position (E_C) of a material relative to the water reduction potential level (H^+/H_2), we carried out the three-step calculation approach of ref. 18. This method is cost efficient compared to other explicit solvation approaches^{20,61} with similar accuracy, although this approach is sophisticated to calculate. To determine the H^+/H_2 acceptor level relative to the average Hartree potential in bulk liquid water (second step in the three-step calculation), classical molecular dynamics (MD) simulations are performed at room temperature using the LAMMPS code⁶² to construct the bulk liquid water structure. The TIP4P/2005 potential⁶³ is employed to describe the atomic configuration and the interaction between water molecules. This TIP4P/2005 potential showed many structural parameters and properties (including density⁶³, thermal expansion coefficient⁶³, diffusivity⁶³, and the structure factor⁶⁴) comparable to the experimental values, at 298 K. Therefore, the potential is enough to describe liquid water structure at 298 K, even though the TIP4P/2005 potential slightly over-structures liquid water⁶³. 140 H_2O molecules are placed in the

simulation cell ($\sim 11 \times 11 \times 27 \text{ \AA}^3$) to mimic the density of liquid water (1 g cm^{-3}) at 298 K and equilibrated within the NVT ensemble for 1000 ps at 298 K¹⁷. The temperature was controlled by a Nosé-Hoover thermostat. The H^+/H_2 acceptor level is determined by substituting an H_3O^+ for one of the 140 H_2O molecules in the optimized bulk liquid water system (H_3O^+ -water), then optimizing the atomic configuration using DFT. Afterwards, the density of states (DOS) of the DFT-optimized H_3O^+ -water is calculated at the Γ k -point with DFT in order to obtain the energy level of the H_3O^+ ion in water (acceptor level of water) as introduced in refs. 17,18.

The TMO/water interfaces ($\approx 10 \times 10 \times 45 \text{ \AA}^3$) are explicitly constructed with direct contact of the slabs and liquid water as illustrated in ref. 17 and Supplementary Fig. 6. No preferential orientation of water molecules at the CoO surface/water interface is observed¹⁷ from the calculation of orientation of water molecules (angle between water dipole moment vector and the surface normal) after *ab initio* MD relaxation, without dissociation of water molecules on the CoO surfaces. On the other hand, a few water molecules on rutile $\text{TiO}_2(001)$ constructed with bulk phase cleaved along (001), are dissociated into OH and H groups and the OH and H groups are adsorbed on the rutile $\text{TiO}_2(001)$ surface (Supplementary Note 3 and Supplementary Fig. 7). Despite the change in the surface chemistry originated from the water dissociation, the E_C vs. H^+/H_2 barely changes (Supplementary Fig. 8) from that of the as-constructed water/rutile $\text{TiO}_2(001)$ interface (at $t = 0$ in the *ab initio* MD relaxation). Therefore, the E_C vs. H^+/H_2 calculated without further ionic relaxation after the construction of the TMO/water interface supercells, is considered to be able to represent the E_C of TMOs obtained after relaxation in water. Thus, the TMO/water supercells are not re-optimized for static DFT calculations. Using static DFT calculations together with various conditions of magnetic configuration or U_{eff} values, the Hartree potentials of the whole system of the TMO/water interfaces are then obtained as a function of position along the thickness direction (from the slab to the water layer).

Also, as observed in experimental results^{65–67}, our *ab initio* MD calculation of various TiO_2 /water interfaces (Supplementary Note 4 and Supplementary Fig. 9a–d) showed that water molecules are dissociated on both rutile and anatase $\text{TiO}_2(001)$ surfaces generated with bulk phase cleaved along (001) (Supplementary Fig. 9a, c), while H_2O molecules keep their forms without dissociation on both rutile $\text{TiO}_2(110)$ and anatase $\text{TiO}_2(101)$ (Supplementary Fig. 9c, d) that are known to be the most stable among various surfaces. Several H_2O molecules (not all H_2O molecules) near the surfaces have the preferred orientation with respect to the surface normal, as shown in Supplementary Fig. 9b, d, which are in the same vein as other theoretical calculations^{68–70}. Thus, it is considered that the size and the structure of our surface/water interface model are optimal to capture and describe the real interactions of the water-water molecules and the water-surface.

Data Availability

The authors declare that all the other data supporting the findings of this study are available within the article and its supplementary information files and from the first author upon request.

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Author contributions

K.W. designed the study, performed the computational experiments, analysed the data and wrote the manuscript with assistance and feedback from A.M.

Additional information

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