Solvation effects on the band edge positions of photocatalysts from first principles: supporting information

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DFT calculation details

We performed first principles calculations of the structural and electronic properties of Si, TiO_2, IrO_2 and WO_3 in vacuum as well as solution using the open-source plane-wave density functional theory software, JDFTx,[1] which implements several solvation models including SaLSA[2] and CANDLE.[3]

We used GBRV[4] ultrasoft pseudopotentials at their recommended kinetic energy cutoffs of 20 and 100 Hartrees for the wavefunctions and charge densities respectively. The Ti, Ir and W pseudopotentials include eight semicore electrons (penultimate *sp* shell) in the valence partition, whereas all other pseudopotentials (Si, C, H and O) only include valence electrons. See Ref. 4 for further details regarding the pseudopotential parameters.

We employed the PBE[5] generalized gradient approximation (GGA) to the exchange-correlation functional, along with the DFT-D2 pair-potential corrections[6] to account for long-range dispersion interactions. We found that the D2 dispersion corrections significantly improve the lattice constants of room temperature (γ)-WO_3 in contrast to those with PBE alone,[7] but have a negligible effect ($< 1\%$) on those of Si, TiO_2 and IrO_2. However, we omit DFT-D2 corrections for Si in this paper in order to more clearly compare our calculations with the published AIMD study[8] that uses the PBE functional without DFT-D2 corrections.

We optimized lattice constants and internal geometries of each bulk material and constructed slabs by appropriately repeating and terminating the bulk geometry. We then constrained the lattice vectors of the slabs in the two periodic directions and fully optimized all atomic positions self-consistently for each calculation, in vacuum as well as in solution. Our geometry optimization uses an L-BFGS algorithm with a downhill cubic line-minimize in JDFTx that can only converge to local minima, and we ensured that the forces of our calculations are fully converged to less than 10^{-4} Hartrees/bohr on each atom. In order to ensure that we capture the lowest energy configuration of the explicit water molecules, we consider several initial configurations and report all the low-energy converged local minima. The geometries of all reported calculations are also included in the supporting information as CIF files.

We used Monkhorst-Pack k-point grids for all the slab calculations: 8×8×1 for the (1×1)-(111) functionalized Si surfaces, 3×6×1 and 5×10×1 respectively for the (1×1)-(110) TiO_2 and IrO_2 surfaces, and 3×3×1 for the $c(2\times2)$-(001) γ-WO_3 surfaces. For supercell surface calculations, we reduced the number of k-points appropriately: 2×2×1 for the (4×3)-(111) Si-$COOH_x$, $p(2\times2)$-(001) γ-WO_3 and $c(4\times4)$-(001) γ-WO_3 surfaces, and 1×1×1 for the $p(2\times2)$-(001) γ-WO_3 surface. We used a smearing of 0.005 Hartrees to resolve the Fermi surface of IrO_2, which is a metal.

Water binding energies

For each surface that we compare to experiment, we examine the effect of including explicit water molecules adsorbed on the surface instead of, and in addition to, the solvation models. We optimized the geometries of the water molecules and the surface starting from several different initial configurations of water and found only two classes of local-energy-minima structures in the surface unit cell, as described in the main text.

We compare the relative stability of the different water configurations using the binding energy per water molecule defined as

$$E^{\mathrm{H_2O}}_{\mathrm{bind}} = (E_{\mathrm{surf}+N\mathrm{H_2O}} - E_{\mathrm{surf}})/N - E_{\mathrm{H_2O}},$$

where $E_{\mathrm{surf+N\ H_2O}}$, E_{surf} and $E_{\mathrm{H_2O}}$ are the energies of a slab calculation with N explicit water molecules adsorbed on the surface, the same slab without any explicit water molecules and an isolated water molecule. In each binding energy calculation, all these energies are calculated with the same method: a vacuum DFT calculation, or a DFT calculation employing the SaLSA or CANDLE solvation models. These binding energies are effectively at zero temperature, but finite temperature corrections (which are

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expensive to calculate) will not change the relative energies between different adsorbate configurations and hence will not alter the relative stabilities inferred in the main text.

The results of these binding energy calculations in vacuum, SaLSA and CANDLE are presented in Tables 2, 3 and 4 of the main text for the TiO_2 (110), IrO_2 (110) and WO_3 (001) surfaces respectively. The binding energies in solution are always lower because solvation stabilizes the isolated water molecule more than the ones adsorbed on the surface. The values computed using CANDLE are slightly smaller than those using SaLSA, by ~ 0.1 eV/H_2O, which is consistent with their similar solvation shifts (within ~ 0.1 eV), as discussed in the main text. Water binds much more strongly to the IrO_2 (110) surface than both the WO_3 (001) and TiO_2 (110) surfaces, and it binds dissociatively with this surface, which correlates well with the higher OER reactivity of IrO_2.

O vacancies on WO_3 (001) surfaces

Predicting accurate O vacancy concentrations theoretically is extremely challenging, because of the exponential sensitivity of concentrations to inaccuracies in DFT formation energies due to the exchange-correlation functional errors and uncertainties in the chemical potential of O in the solid. Therefore, theoretical studies of vacancies in compound semiconductors conventionally focus on *trends* in formation energies rather than their absolute values, and report results for upper and lower bounds of the chemical potential.[9] In the present case, the O chemical potential is bounded by the O-rich limit where the O reservoir is molecular oxygen, so that $\mu_O^{\text{rich}} = \frac{1}{2}E_{O_2}$, and by the O-poor limit where the reservoir is the oxide itself, so that $\mu_O^{\text{poor}} = \frac{1}{3}\left(E_{WO_3}^{\text{bulk}} - E_W^{\text{bulk}}\right)$. Here, E_{O_2} is the ground state energy of an isolated oxygen molecule, and $E_{WO_3}^{\text{bulk}}$ and E_W^{bulk} are the ground state energies per formula unit of bulk solid tungsten oxide and tungsten respectively. In the case of surface vacancies in solution, liquid water can also act as an O reservoir with chemical potential $\mu_O^{H_2O} = E_{H_2O} - E_{H_2}$. In fact, we find $\mu_O^{H_2O} > \mu_O^{\text{poor}}$ which implies that water provides O more easily than the oxide, so the O-poor limit in solution is set by $\mu_O^{H_2O}$ instead. Here we neglect zero-point vibrational energy, which typically changes the absolute values of the O vacancy formation energies by ~ 0.1 eV,[10] but does not affect the relative formation energies that are important in the discussion of the results in Table 5 of the main text.

Table 5 in the main text compares the formation energy of O vacancies in bulk WO_3 as well as on the (001) surfaces in vacuum and solution. For the surface vacancies, $p(2 \times 2)$ corresponds to half the on-top O missing relative to the stable stoichiometric $c(2 \times 2)$ reconstructed surface (which has O atoms on top of half of the W surface atoms to begin with), $c(4 \times 4)$ has a quarter and $p(4 \times 4)$ an eighth of the surface O missing (see Figure 5 of the main text). The vacancy formation energies decrease with decreasing vacancy concentration in all cases due to unfavorable vacancy-vacancy interactions, but converge to a finite value close to the lowest concentrations (largest supercell calculation) considered here.* The formation energy of bulk O vacancies in WO_3 is positive and $\gtrsim 1$ eV over the entire range of O-rich to O-poor conditions, which indicates that O vacancies are thermodynamically unfavorable and will have very low equilibrium concentrations in the bulk. (Kinetic effects can lead to a larger non-equilibrium concentration in experiment.)

The formation energies of surface vacancies in vacuum are much smaller than the bulk case, by about 2 eV, as Table 5 in the main text shows. The energy penalty of forming surface vacancies is lower because fewer W-O bonds need to be broken at the surface compared to the bulk. In particular, the formation energy of the surface O vacancy becomes negative in the O-poor limit (similar to the results of Ref. 11), indicating that O deficiency could be thermodynamically favorable in the extremely O poor condition, which partially explains the experimental observation of highly O-deficient surfaces prepared by ion bombardment and subsequent annealing in UHV.[12,13]

With surface vacancies in solution, the surface W atoms without on-top O would prefer to form new W-O bonds with water molecules. These bonds would stabilize the surface vacancies further, but solvation models cannot capture the effect of these bonds, so we always use a layer of explicit H_2O molecules in these calculations in addition to the CANDLE solvation model.† Consequently, the surface with vacancies will have an extra H_2O molecule (per vacancy) compared to the surfaces without. Therefore the formation energy calculation requires the chemical potential for water molecules as well, which we set to the free energy of a water molecule in liquid water, which is in turn equal to the isolated molecule energy plus the solvation free energy of 6.0 kcal/mol.[14] Table 5 in the main text shows that the formation energies of O vacancies on WO_3 (001) surfaces in solution are further stabilized by $0.1 - 0.4$ eV compared to those in vacuum. Indeed, we

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*Fully converging these results (e.g. to less than 0.1 eV) with supercell size requires tremendous computational effort, and is not necessary as the relevant trends are apparent at the present level of convergence.

†We use only one solvation model – the slightly cheaper CANDLE model – for these large supercell calculations; previous results in this section indicate that the SaLSA model would produce very similar results within 0.1 eV.

can expect higher concentrations of O vacancies on the solvated surfaces.

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