Supporting Information for “Energetics and solvation effects at the photoanode-catalyst interface: Ohmic contact versus Schottky barrier”

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¶The University of Chicago
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1. Computational details of DFT calculations

Calculations of the structural and electronic properties of WO$_3$ and IrO$_2$ using the PBE$^1$ and PBE+D2$^2$ approximations were carried out with the Quantum Espresso package,$^3$ using ultrasoft pseudopotentials;$^4$ the eight (5s, 5p) electrons of Ir(W) were included in the valence partition. A kinetic energy cutoff of 40Ry for the wavefunction and of 200 Ry for the density together with a (10x10x12)/(3x3x3) Monkhorst-Pack k-point grid were used in the geometry optimizations and single point calculations of IrO$_2$/room temperature($\gamma$)-monoclinic WO$_3$. In the case of IrO$_2$ which is a metal, we applied a finite smearing$^5$ of 0.02 Ry to the computed eigenvalues, so as to improve the k point convergence for bulk IrO$_2$ and for the interface calculations. To optimize the cell parameters and the internal geometry of all crystal structures (variable cell calculations), we used a smooth kinetic-energy cutoff scheme.$^6$

We computed the lattice constants of WO$_3$ with several different exchange correlation functionals and compared the electronic band gaps computed at the experimental geometry and at the optimized geometry of each functionals; these are shown in Table S1. The local density functional (LDA) approximation gives the best lattice constants, compared with the experiment; however, the band gap computed at the experimental and optimized geometries differ by 0.57 eV, due to the LDA underestimation of lattice distortions (i.e. LDA overestimates the octahedra tilt angles). By including an empirical long range vdW-dispersion interaction term (D2)$^2$ on top of the Perdew-Burke-Ernzerhof$^7$ functional, we found improved lattice constants with respect to PBE and other functionals, although still worse than those computed at the LDA level of theory; however the band gaps obtained at the ex-
Table S1: Equilibrium lattice parameters ($a_0, b_0, c_0$) of $\gamma$-monoclinic WO$_3$ and its band gap ($E_g$) at the experimental (Exp.) geometry ($V_{\text{exp}}$) and the geometry optimized within density functional theory ($V_{\text{DFT}}$). The ranges of measured photoemission (P.E.) and optical gaps (Opt.) are given at the top of column 7. The various functionals used are given in column 1. LDA and PBE calculations were carried out with LDA and PBE pseudopotentials, respectively. vdW-DF2, PBEsol and PBE+D2 calculations were carried out with PBE poseudopotentials. The B3PW calculation was performed using the Crystal code with angular momentum projected core effective potentials (Hay-Wadt) to replace the deeper core electrons of W (all electrons were included for the O atom). The basis sets for W and O atoms were the same as Ref. 11. $\beta$ is the angle between the $a$ and $c$ axes, and $\Delta V$ is the relative difference between the computed and the experimental volumes. The details of G$_0$W$_0$@PBE+D2 were explained in Ref. 12 and Section 4 in SI.

<table>
<thead>
<tr>
<th>Method</th>
<th>Lattice parameters (Å)</th>
<th>$\beta$ (°)</th>
<th>$\Delta V$ (%)</th>
<th>$E_g$ (eV)</th>
<th>$E_g$ (P.E.)</th>
<th>$E_g$ (Opt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.$^{13}$</td>
<td>7.306 7.540 7.692 90.88</td>
<td>3.38±0.2</td>
<td>2.6-2.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDA$^{16}$</td>
<td>7.35 7.45 7.66 90.6</td>
<td>-0.9</td>
<td>1.87</td>
<td>1.97</td>
<td>1.53</td>
<td></td>
</tr>
<tr>
<td>PBE$^{1}$</td>
<td>7.44 7.67 7.77 90.6</td>
<td>4.5</td>
<td>1.92</td>
<td>1.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>vdW-DF2$^{17}$</td>
<td>7.54 7.56 7.77 90.8</td>
<td>4.6</td>
<td>2.04</td>
<td>1.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBEsol$^{18}$</td>
<td>7.60 7.52 7.69 90.0</td>
<td>3.9</td>
<td>1.92</td>
<td>1.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE+D2$^{2}$</td>
<td>7.42 7.36 7.54 91.9</td>
<td>-2.8</td>
<td>1.98</td>
<td>1.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3PW$^{19}$</td>
<td>7.42 7.68 7.85 90.0</td>
<td>5.7</td>
<td>3.32</td>
<td>3.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G$_0$W$_0$@PBE+D2</td>
<td>7.42 7.36 7.54 91.9</td>
<td>-2.8</td>
<td>3.30</td>
<td>3.27</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experimental and the optimized (PBE+D2) geometries differed only by 0.02 eV. These results are consistent with findings reported in the literature about the importance of including van der Waals interactions to obtain a correct lattice energy in WO$_3$. Interestingly, the lattice constants of IrO$_2$ are rather insensitive to the choice of functionals as shown in Table S2. Therefore, we used PBE+D2 for most of the DFT calculations in this paper.

2. Surface energy of WO$_3$ and IrO$_2$ surfaces

Surface energies were computed by subtracting from the total energy of the slab the bulk total energy, as obtained from separate calculations. With increasing number of layers in the slab, the surface energy converges to a constant value $\sigma$ per unit cell, which can be expressed...
Table S2: Equilibrium lattice parameters \((a_0, b_0)\) of IrO\(_2\). LDA(PBE) denotes the results of calculations carried out using the local density (PBE) functional; “PBE+D2” denotes the results of calculations carried out using PBE functional with an empirical long range vdw-dispersion interaction correction;\(^2\) and “Exp” denotes the experimental values from Ref 20. \(\Delta V\) is the relative difference between the computed and the experimental volumes and \(u\) denotes the internal coordinates of IrO\(_2\): Ir (0, 0, 0) and (0.5, 0.5, 0.5); O +/- (u, u, 0) and +/- (0.5+u, 0.5-u, 0.5).

<table>
<thead>
<tr>
<th>Method</th>
<th>Lattice parameters (Å)</th>
<th>(\Delta V) (%)</th>
<th>(u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.(^{20})</td>
<td>4.50 3.16</td>
<td>-</td>
<td>0.3077</td>
</tr>
<tr>
<td>LDA(^{16})</td>
<td>4.46 3.12</td>
<td>-3.0</td>
<td>0.3080</td>
</tr>
<tr>
<td>PBE(^{1})</td>
<td>4.54 3.18</td>
<td>2.2</td>
<td>0.3083</td>
</tr>
<tr>
<td>PBE+D2(^{2})</td>
<td>4.50 3.18</td>
<td>0.7</td>
<td>0.3086</td>
</tr>
</tbody>
</table>

as:

\[
\sigma = \frac{1}{2}(E_{slab}^n - nE^{bulk})
\]  

where \(E_{slab}^n\) is the total energy of an \(n\)-layer slab and \(E^{bulk}\) is the bulk energy per layer of an infinite solid. The factor of one half takes into account the two surfaces present in the slab. We found that 4 layers for WO\(_3\) and 5 layers for IrO\(_2\) suffice to converge the surface energy within 0.02 \(J/m^2\) at fully optimized geometries. We built symmetric slabs for all the surfaces considered here, to avoid the presence of net dipoles in the supercells.

### 2.1 Surface energy of WO\(_3\) surfaces

Both (100) and (001) thin films were experimentally prepared and results reported in the literature.\(^{21-26}\) It is known that WO\(_3\) thin films tend to lose oxygen at the surface and a \((\sqrt{2}\times\sqrt{2})\)R45\(^\circ\)(or c(2\times2)) reconstructed (001) surface was observed by low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM).\(^{21-24}\) The surface energies of several simple cubic WO\(_3\) surfaces were also reported in the literature.\(^{27}\) In the following we compared the surface energy of several \(\gamma\)-monoclinic WO\(_3\) surfaces.
Table S3 show the surface energy of several stoichiometric $\gamma$-monoclinic $\text{WO}_3$ surfaces. For the (001), (100), (010) surfaces, we considered the $(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ reconstruction which in all cases has a lower surface energy than a $(2 \times 2)$ reconstruction. For the (110), (011), (101) surfaces, we considered instead the $(2 \times 2)$ reconstruction with one O atom on top of each W surface atom, similar to the corresponding (110) surface of simple cubic $\text{WO}_3$ reported in Ref. 27. We did not consider the (111) $\text{WO}_3$ surface which likely has a much higher energy than those of Table S3, due to three W-O broken bonds for each surface W atom. We found that the (001), (100), (010) surfaces, which have similar structures, have lower energies than the (110), (011), (101) ones. However, the surface energies of (001) and (100) are rather similar differing by only 0.05 J/m$^2$.

Table S3 : Surface energy (J/m$^2$) of several stoichiometric $\text{WO}_3$ surfaces computed at the PBE and PBE+D2 levels of theory.

<table>
<thead>
<tr>
<th>Method</th>
<th>(001)</th>
<th>(100)</th>
<th>(010)</th>
<th>(011)</th>
<th>(110)</th>
<th>(101)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>0.273</td>
<td>0.237</td>
<td>0.323</td>
<td>0.675</td>
<td>0.774</td>
<td>0.765</td>
</tr>
<tr>
<td>PBE+D2</td>
<td>0.597</td>
<td>0.635</td>
<td>0.976</td>
<td>1.021</td>
<td>1.102</td>
<td>1.098</td>
</tr>
</tbody>
</table>

2.2 Surface energy of $\text{IrO}_2$ surfaces

The surfaces of $\text{IrO}_2$ have not yet been systematically studied. $\text{IrO}_2$ has a rutile structure very similar to that of rutile $\text{TiO}_2$, whose surfaces have been extensively studied.$^{28-31}$ We constructed stoichiometric $\text{IrO}_2$ surfaces similar to the corresponding ones of stoichiometric rutile $\text{TiO}_2$ surfaces, following Refs 29,30. Similar to the (110) $\text{TiO}_2$ surface, the (110) $\text{IrO}_2$ surface has the lowest surface energy (as shown in Table S4), due to the high coordination number of Ir atoms compared to other surfaces. We note that the surface energy of (110) $\text{IrO}_2$ is significantly larger than that of stoichiometric rutile $\text{TiO}_2$ (0.5 J/m$^2$ at PBE$^{32}$), but it is similar to that of another OER catalyst, i.e. $\text{RuO}_2$ (1.14 J/m$^2$ at PBE$^{33}$). This high surface energy is likely related to the excellent catalytic activity for water oxidation. We found that the trend of the surface energies as a function of surface orientations is the same.
in IrO₂ and TiO₂.³⁰

Table S4: Surface energy (J/m²) of several stoichiometric IrO₂ surfaces computed at the PBE and PBE+D2 levels of theory.

<table>
<thead>
<tr>
<th>Method</th>
<th>(001)</th>
<th>(100)</th>
<th>(110)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>2.392</td>
<td>1.878</td>
<td>1.437</td>
<td>1.889</td>
</tr>
<tr>
<td>PBE+D2</td>
<td>3.035</td>
<td>2.640</td>
<td>2.117</td>
<td>2.622</td>
</tr>
</tbody>
</table>

3. Band alignment at the (110)WO₃/(111)IrO₂ interface

In addition to the (001)WO₃/(111)IrO₂ interface, formed by joining the most energetically favorable surfaces, we also considered the interface with the smallest lattice mismatch between the two solids: (3x3)-(110)WO₃/(8x8)-(111)IrO₂; this interface exhibits less than 2% lattice mismatch between two constituent surfaces. We fixed the lattice constant along the lateral directions (x,y) to that of WO₃ and optimized the lattice constant along the direction perpendicular to the interface. The internal geometry was fully optimized as well. We made numerous attempts to construct a WO₃(110)/(111)IrO₂ interface with lower energy. For example, we translated the IrO₂ lattice in either the x or y directions by 1 Å, and we optimized the interface geometry again, but this led to a higher energy. We also compressed the interface along the z direction by 1 Å, but upon optimization the energy increased again. The final interface structure is shown in Fig.S1.

In this geometry, all the Ir atoms are five-fold coordinated instead of six-fold coordinated as in the case of the (001)WO₃/(111)IrO₂ interface; furthermore some O belonging to WO₃ are not bonded to the IrO₂ surface. This less favorable coordination is responsible for a higher interface energy by 0.65 J/m² with respect to the (001)WO₃/(110)IrO₂ interface, despite of the smaller lattice mismatch.

Interestingly, the band alignment found for (001)WO₃/(110)IrO₂ and (110)WO₃/(111)IrO₂ are similar. We have computed the band alignment of the latter following the same pro-
procedure as discussed in the main text; we found $\phi_{SB} = E_{CBM} - WO_3 - E_{F_{interface}} = -0.45$ eV for the (110)WO$_3$/(111)IrO$_2$ interface to be compared with the value of -0.32 eV for the (001)WO$_3$/(110)IrO$_2$ interface.

Figure S1 : Atomistic model of the (110)WO$_3$/(111)IrO$_2$ interface. The red, green and silver spheres represent O, Ir, W atoms, respectively.

4. Computational details of $G_0W_0$ calculations

In $G_0W_0$ calculations, the quasiparticle energy correction $\Delta E_{n,k}$ to a DFT orbital $\phi_{n,k}$ was obtained as:

$$\Delta E_{n,k} = Z_{n,k} \langle \phi_{n,k} | \Sigma(E_{n,k}^{DFT}) - V_{x,c}^{DFT} | \phi_{n,k} \rangle$$

where $\Sigma$ is the self energy of electrons within the GW approximations; $V_{x,c}^{DFT}$ is the exchange-correlation potential from DFT; n, k are the band and k point indeces; $Z_{n,k} = (1 - \partial \Sigma / \partial E)^{-1} \big|_{E=E_{n,k}^{DFT}}$. 

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The GW self energy $\Sigma$ can be formally written in real space as:

$$\Sigma(r, r', E) = \frac{i}{2\pi} \int dE' e^{-i\delta^{+}E'} G(r, r'; E - E') W(r, r'; E')$$

Here $G$ is the Green’s function of the electrons and $W$ is the dynamically screened Coulomb potential, and equals the bare Coulomb potential multiplied by the inverse dielectric matrix $\epsilon^{-1}(r, r', E)$; $\delta^{+}$ is a positive infinitesimal time.

The frequency dependence of the dielectric matrix was modeled using a generalized plasmon pole model (GPP)\textsuperscript{34} for both WO$_3$ and IrO$_2$. The computational details of $G_0W_0$ calculations of WO$_3$ were reported in Ref 12. We used the same numerical parameters and implementation as in Ref 12 and we recomputed the $G_0W_0$ correction to the DFT orbitals obtained with the PBE+D2 functional using the fully optimized geometry at the same level of theory. The $G_0W_0$ correction to the CBM of WO$_3$ at the PBE+D2 is 0.95 eV using the GPP model, which differs by 0.05 eV from the result obtained by a full frequency integration.

We note that we computed the band gap of WO$_3$ is 1.98 eV (1.96 eV) using PBE+D2 at the experimental geometry (the optimized geometry); 3.30 eV (3.27 eV) using G$_0$W$_0$@PBE+D2 at the experimental geometry (the optimized geometry of PBE+D2); and 3.32 eV (3.03 eV) using B3PW91 at the experimental geometry (the optimized geometry). We have shown in Ref 12 that it is necessary to take into account the relativistic effect, the electron phonon interaction contribution to the band edge position and include the exciton binding energy, in order to obtain a good agreement between the band gap computed within many body perturbation theory and the measured optical gap (2.6 eV).

We now turn to IrO$_2$. To verify the validity of the GPP model, we performed some of our calculations with a full frequency integration method; for example, we used a contour deformation method\textsuperscript{35} as implemented in the ABINIT code;\textsuperscript{36} the Fermi level of IrO$_2$ obtained by full frequency integration was found to be 0.17 eV higher than the one computed using the GPP model. For computational simplicity, we used the GPP models in our interface
calculations, keeping in mind that the work function of IrO$_2$ may be inaccurate by $\sim 0.2$ eV.

In our $G_0W_0$ calculations we used 12 Ry to represent the dielectric matrix and the correlation part of the self energy (the eigenvalues were converged within 1 meV compared to calculations using 60 Ry); we instead used 80 Ry for the evaluation of the exchange part of the self energy and 80 Ry to represent the ground state wave functions. We employed 6x6x8 k point grids for the Brillouin zone integration. We did not include intraband transitions in the calculations of the head of the dielectric matrix, which appears to lead to minor inaccuracies in the case of IrO$_2$: indeed we did not observe an artificial gap opening around the Fermi level due to the neglect of intraband transitions, unlike the case, e.g. metal sodium.$^{37}$

![Figure S2](image_url)

**Figure S2 :** $G_0W_0$ corrections (dots) to the Fermi level of IrO$_2$ obtained with semi-local DFT (PBE), computed as a function of the number of bands ($N_{\text{bands}}$) included in the calculations. The results are fitted using the functional form described in the text and displayed in red [$E(N) = E_0 - b/N$].

The convergence of our calculations with the number of bands entering the expressions of the dielectric matrix and the self energy was carefully tested: we extrapolated the number of bands to infinity with the empirical form $E(N) = E_0 - b/N$ (as shown in Fig. S2);
the Fermi level computed with 400 bands differed from the extrapolated value by 0.16 eV. The converged value of the Fermi level obtained in our $G_0W_0$ calculation is 1.70 eV higher than the one computed at the PBE+D2 level of theory (we note that the vDW dispersion correction(D2) to the PBE functional does not affect the position in energy of the electronic states at fixed geometry).

5. Computational details of the charge netruality level

We computed the charge neutrality level (CNL) of bulk WO$_3$ by the method proposed using Tersoff;\textsuperscript{38} the CNL is defined as the energy $E_{CNL}$ where the real space Green’s function $G(\vec{R}, E)$ changes sign: $G(\vec{R}, E) = \frac{\rho_{\vec{R}}}{\rho_{n,k}}$, where $n$ and $k$ are the bulk band and k point indeces respectively; $E_{nk}$ is the eigenvalues of the bulk states; $\vec{R}$ is a real space vector pointing to the surface. We obtained $E_{CNL}=0.80$ eV below the conduction band minimum (CBM) of WO$_3$. We used a scissor operator to rigidly shift the conduction states and open a band gap equal to that computed at the $G_0W_0@PBE + D2$ level of theory (3.27 eV); thus the computed value of the CNL is closer to the CBM than the VBM.

6. Electrostatic potential profile of the WO$_3$/IrO$_2$ interface

In Fig. S3 we show the planar average of the electrostatic potentials computed independently for bulk WO$_3$ (orange curve) and bulk IrO$_2$ (blue curve); their values coincide with those of the respective bulk regions of the (001)WO$_3$/(110)IrO$_2$ interface model (black curve). These results show that the electronic structure of the two bulk portions is well converged with respect to the number of atomic layers used in our model.
Figure S3: The planar average of the electrostatic potential of bulk IrO$_2$ (blue curve), bulk WO$_3$ (orange curve) and of the (001)WO$_3$/(110)IrO$_2$ interface model (black curve) along the direction ($z$) perpendicular to the interface. The electrostatic potentials of bulk IrO$_2$ and WO$_3$ are shifted so as to be aligned with that of the corresponding bulk region at the interface.

References


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(6) Bernasconi, M.; Chiarotti, G. L.; Focher, P.; Scandolo, S.; Tosatti, E.; Parrinello, M. 


