DFT study of various tungstates for photocatalytic water splitting

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Electronic Supplementary Information

Table S1 Optimised lattice parameters, equilibrium volume, and band gap of monoclinic WO_3 , α -Sn WO_4 and Bi_2WO_6 calculated with five different functionals; experimental values (measured at room temperature) are included for comparison.

| Compound | Functional | a (Å) | <i>b</i> (Å) | <i>c</i> (Å) | β(°) | Volume (Å ³ /cell) | Band gap (eV) |
|---------------------------------|---------------------------|-------|--------------|--------------|------|----------------------------------|---------------|
| WO ₃ | B3LYP | 7.45 | 7.74 | 7.93 | 90.1 | 57.2 | 2.91 |
| | B3PW | 7.40 | 7.67 | 7.87 | 90.2 | 55.9 | 3.02 |
| | PBE0 | 7.33 | 7.61 | 7.82 | 90.6 | 54.5 | 3.67 |
| | HSE06 | 7.33 | 7.58 | 7.81 | 90.6 | 54.2 | 2.98 |
| | HSEsol | 7.26 | 7.47 | 7.69 | 91.0 | 52.1 | 2.99 |
| | Experimental ³ | 7.30 | 7.54 | 7.69 | 90.9 | 53.0 | 2.6-3.0 |
| α-SnWO ₄ | B3LYP | 5.70 | 11.65 | 5.08 | - | 84.3 | 2.15 |
| | B3PW | 5.63 | 11.58 | 4.99 | - | 81.3 | 2.02 |
| | PBE0 | 5.67 | 11.45 | 5.10 | - | 82.7 | 3.31 |
| | HSE06 | 5.61 | 11.55 | 4.98 | - | 80.7 | 1.65 |
| | HSEsol | 5.54 | 11.50 | 4.91 | - | 78.2 | 1.28 |
| | Experimental ⁴ | 5.63 | 11.65 | 4.99 | - | 81.8 | 1.6-1.9 |
| Bi ₂ WO ₆ | B3LYP | 5.59 | 15.12 | 5.56 | - | 117.5 | 3.12 |
| | B3PW | 5.63 | 16.82 | 5.62 | - | 133.0 | 2.89 |
| | PBE0 | 5.67 | 16.33 | 5.53 | - | 128.0 | 3.82 |
| | HSE06 | 5.54 | 16.43 | 5.57 | - | 126.7 | 2.83 |
| | HSEsol | 5.62 | 16.82 | 5.81 | - | 137.3 | 3.03 |
| | Experimental ⁵ | 5.44 | 16.43 | 5.46 | - | 122.0 | 2.80 |

It can be seen from the side view of the bulk structure of WO₃ (Fig. S1(a)) that there are two kinds of layers that alternate along the [001] direction – a layer of oxygen atoms and a layer with a composition of WO₂. Thus, a dipole across the slab will result if a slab is produced by cleaving between any two adjacent layers (i.e. there will be a layer containing only oxygen atoms on the top surface of the slab but no corresponding layer of only oxygen atoms on the bottom surface, Fig. S1(b)). To remove this dipole, half of the oxygen atoms were moved from the top surface to the bottom surface, resulting in a symmetric slab (Fig. S1(c)).



Fig. S1 (a) Side view of the optimised bulk structure of WO_3 aligned so that the [001] direction is vertical; (b) side view of the optimised structure of a slab cleaved from the bulk structure to expose the (001) surface with a thickness of three atomic layers; cutting the slab in this way produces a dipole; (c) as for (b) but with the dipole removed by moving half of the oxygen atoms from the top surface to the bottom surface (the atoms indicated by the circle were used for calculating the oxygen 1s orbital energies in the band energy calculation); (d) as for (c) but with a thickness of five atomic layers. Red spheres represent O atoms and grey spheres represent W atoms.

For the calculation of band energies, the O 1s orbital energy in bulk WO₃ was calculated from the oxygen atoms in the layer with a composition of WO₂ in bulk WO₃ along the [001] direction; the calculated average energy was found to be -523.34 eV. For the calculation of band energies using the slab model, the slab used must be thick enough to avoid any influence on the orbital energies for atoms in the centre of the slab due to the surfaces. To check this, slabs with thicknesses of one atomic layer, three layers and five layers were built for bulk WO₃ (Fig. S1c and S1d). A similar result for the oxygen 1s orbital energy was obtained for the slabs with thicknesses of three and five layers; for both of them, the 1s orbital energy for O atoms in the centre of the slab was found to be -520.91 eV. Thus, a slab thickness of 3 layers was considered to be sufficient. The lowest energy surface of WO₃ was found to be (001) (Table S2). This is in agreement with previous work, in which a ($\sqrt{2} \times \sqrt{2}$) *R*45° reconstructed slab cleaved from the optimised bulk structure to expose the (001) surface was found to give the lowest surface energy.¹ This reconstructed slab was also tested in this work and was found to give the same surface energy as the primitive slab to within 0.01 J/m². Similarly, other previous work has found that the (001) surface has the lowest energy for both the cubic and monoclinic phases of WO₃.²

Table S2 Surface energies for monoclinic WO₃, orthorhombic α -SnWO₄, monoclinic FeWO₄, orthorhombic Bi₂WO₆, Sb₂WO₆, WO₃·H₂O and WO₃·2H₂O. The red text highlights the lowest surface energy for each compound.

| Compound | Surface Energies for different facets (J/m^2) | | | | | | | | | |
|-----------------------------|---|-------|-------|-------|-------|-------|-------|--|--|--|
| Compound | (100) | (010) | (001) | (011) | (101) | (110) | (111) | | | |
| WO ₃ | 0.54 | _ | 0.32 | - | - | 0.52 | 0.47 | | | |
| α -SnWO ₄ | 0.43 | - | 0.51 | - | 0.27 | - | - | | | |
| FeWO ₄ | - | 1.15 | 1.49 | 1.42 | 1.27 | - | - | | | |
| Bi_2WO_6 | 0.69 | 1.49 | - | - | - | - | - | | | |
| Sb_2WO_6 | 0.44 | 0.28 | - | - | 0.39 | - | - | | | |
| $WO_3 \cdot H_2O$ | 0.33 | 0.27 | 0.98 | 0.90 | 0.48 | - | - | | | |
| $WO_3 \cdot 2H_2O$ | - | 0.28 | - | - | - | - | - | | | |



Fig. S2 Side view of the optimised structures of the most stable slabs used in this work. The oxygen atoms that are circled are the ones used in the calculations of the band energies.



Fig. S3 Projected DOS for (a) O 2p and W 5d orbitals for monoclinic WO₃, (b) the Sn 5s, Sn 5p, O 2p and W 5d orbitals for bulk orthorhombic α -SnWO₄ and (c) the Fe 3d, O 2p and W 5d orbitals for bulk monoclinic FeWO₄.

Fig. S4 shows the highest occupied crystalline orbital (HOCO) and the lowest unoccupied crystalline orbital (LUCO) of WO₃, FeWO₄ and Bi₂WO₆. It can be seen from Fig. S4(a) that the O 2p orbitals and W 5d orbitals contribute to both the highest occupied crystalline orbital (HOCO) and the lowest unoccupied crystalline orbital (LUCO) in WO₃, consistent with the projected densities of states shown in Fig. 1(b). For FeWO₄ (Fig. S4(b)), the HOCO has contributions from both O 2p and Fe 3d orbitals but it is mainly formed by Fe 3d orbitals and the LUCO is composed of O 2p, W 5d and Fe 3d orbitals. In contrast, for Bi₂WO₆ (Fig. S4(c)), it can be seen that the HOCO is mainly composed of O 2p orbitals. This difference between the orbitals contributing to the HOCO of FeWO₄ and Bi₂WO₆ is consistent with the projected densities of states (Fig. 3(d) and Fig. 5(c)).



Fig. S4 The highest occupied crystalline orbital (HOCO) and the lowest unoccupied crystalline orbital (LUCO) of (a) WO_3 , (b) FeWO₄ and (c) Bi_2WO_6 . Red, blue, brown and pink spheres represent O, W, Fe and Bi atoms, respectively.



Fig. S5 Relationship between the conduction band energy (vs. NHE) of the ternary tungstates and the distance between two adjacent layers of WO_6 octahedra; the dashed line is a linear fit of the data and serves to guide the eye.

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