SUPPORTING INFORMATION

WO$_3$/BiVO$_4$ Photoanodes: Facets Matching at the Heterojunction and BiVO$_4$ Layer Thickness Effects

Ivan Grigioni,†, I Giovanni Di Liberto, ‡, I Maria Vittoria Dozzi,† Sergio Tosoni,‡ Gianfranco Pacchioni,‡ and Elena Selli*,†

† Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy
‡ Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, via Cozzi 55, 20125 Milano, Italy
I These authors contributed equally
* Corresponding author
E-mail: elena.selli@unimi.it

1. Cross sectional FESEM images and extinction coefficient of BiVO$_4$
2. Supporting XRD analyses
3. Supporting DFT calculations
1. Cross section FESEM images and extinction coefficient of BiVO₄

![Cross section FESEM images](image)

**Figure S1.** Cross section FESEM images (a) of clean FTO and of BiVO₄ photoanodes prepared by successive deposition of (b) 2, (c) 4 and (d) 6 BiVO₄ layers. The scale bar is 500 nm.

We performed the FESEM cross section analysis of the films prepared by 2, 4 and 6 successive BiVO₄ depositions (Figure S1); the cross section of the clean conductive glass substrate was used to determine the thickness of the pristine FTO layer. From the absorption spectra of the three electrodes, reported in Figure 2, and the evaluated thickness of the BiVO₄ overall layers in BiVO₄ photoanodes, we calculated the absorption coefficient of BiVO₄ at 420 nm ($\alpha_{420}$) using the following equation: $A_{420} = \alpha_{420} \times d$, where $d$ is the average thickness in cm and $A_{420}$ the absorbance at 420 nm (Figure 2A). The absorption coefficient $\alpha_{420} = 6.7 \times 10^4$ cm⁻¹ was obtained as the slope of the absorbance at 420 nm vs. film thickness plot shown below.

![Absorbance vs. Thickness](image)
The calculated $\alpha_{420}$ allowed us to estimate the thickness of the individual BiVO$_4$ films (either deposited on FTO or on FTO/WO$_3$) from the electrode absorbance at 420 nm. The thickness of the BiVO$_4$ layer was found to increase almost linearly with the number of coated layers with an average increment of ca. 20 nm per coated layer, as shown by the data reported in Table S1.

**Table S1.** Absorbance (Abs) at 420 nm and thickness of the BiVO$_4$ layers in single BiVO$_4$ and composite WO$_3$/BiVO$_4$ photoanodes, obtained upon deposition of a different number of BiVO$_4$ coated layers.

| Coatings | BiVO$_4$ Abs | BiVO$_4$ Thickness (nm) | WO$_3$/BiVO$_4$ Abs | WO$_3$/BiVO$_4$ Thickness (nm) |
|----------|--------------|-------------------------|----------------------|--------------------------------|
| 1        | 0.09         | 14                      | 0.11                 | 16                             |
| 2        | 0.21         | 31                      | 0.20                 | 30                             |
| 3        | 0.33         | 49                      | 0.33                 | 50                             |
| 4        | 0.50         | 75                      | 0.50                 | 74                             |
| 6        | 0.76         | 114                     | 0.77                 | 115                            |
| 8        | 1.09         | 163                     | 1.07                 | 160                            |

2. Supporting XRD analyses

**Figure S2.** XRD patterns of (A) the BiVO$_4$ and (B) the WO$_3$/BiVO$_4$ photoanodes series. The reflections of BiVO$_4$ and WO$_3$ monoclinic scheelite, as well as those of FTO, are indicated with B, W and FTO, respectively. Insets: intensity of the peak at 27.3° vs. the number of coated BiVO$_4$ layers.
3. Supporting DFT calculations

3.1 Cutoff limits, convergence criteria and thresholds, and reciprocal space sampling

The cutoff limits in the evaluation of Coulomb and exchange series were set to $10^{-7}$ for both Coulomb overlap and penetration, $10^{-7}$ for exchange overlap and pseudo-overlap in the direct space, and $10^{-14}$ for exchange pseudo-overlap in the reciprocal space. An SCF was considered converged when the energy difference between two consecutive steps was below $10^{-6}$ au. The reciprocal space of heterostructure models was sampled by adopting a working shrinking factor equal to 4. For all atoms, the thresholds for the maximum and the root mean square forces were set to 0.00045 and 0.00030 au and those for the maximum and the root mean square atomic displacements to 0.00180 and 0.00120 au, respectively.

3.2 Results

a. Bulk WO$_3$ and BiVO$_4$

The calculated bulk structural and electronic properties of WO$_3$ and BiVO$_4$ are reported in Table S2, in comparison with available experimental data.

|          | a / Å  | b / Å  | c / Å  | β / degrees | $E_g$ / eV |
|----------|--------|--------|--------|-------------|------------|
| WO$_3$ [DFT] | 7.345  | 7.617  | 7.816  | 90.5        | 2.98       |
| WO$_3$ [Exp.] | 7.306  | 7.540  | 7.692  | 90.9        | 2.6-3.2    |
| BiVO$_4$ [DFT] | 7.215  | 11.544 | 5.093  | 134.9       | 3.23       |
| BiVO$_4$ [Exp.] | 7.258  | 11.706 | 5.084  | 134.1       | 2.4-2.5    |

b. WO$_3$ (001) and BiVO$_4$ (010) surfaces

The fully optimized bulk structures have been used to design surface models. We designed a WO$_3$ (001) 1.6 nm thick slab which ensures a good convergence of surface properties,
and variously sized BiVO₄ (010) slabs, with a thickness ranging from 1.1 to 3.3 nm. The calculated structural and electronic properties of fully optimized slabs models are reported in Table S3.

Table S3. Relaxed lattice parameters (a, b, γ), surface energy (Eₛ, with respect to the bulk) and band gap (E₉) of WO₃ and BiVO₄ slabs used to design the interface models.

| system          | Thickness / nm | a / Å  | b / Å  | γ / degrees | Eₛ / J m⁻² | E₉ / eV |
|-----------------|----------------|--------|--------|-------------|------------|--------|
| WO₃ (001)       | 1.6            | 7.311  | 7.382  | 90.0        | 0.37       | 2.86   |
| BiVO₄ (010)     | 1.1            | 4.989  | 5.258  | 89.5        | 0.35       | 3.51   |
|                 | 2.2            | 5.023  | 5.219  | 89.8        | 0.36       | 3.38   |
|                 | 3.3            | 5.036  | 5.202  | 90.0        | 0.37       | 3.33   |
|                 | 3.3 (√2; √2)ᵃ  | 7.240  | 7.240  | 88.1        | 0.37       | 3.33   |
| BiVO₄ (110)     | 2.8            | 5.084  | 6.842  | 112.6       | 0.45       | 3.23   |

ᵃ This cell is obtained by a rotation of 45° with respect to the standard crystallographic orientation.

c. WO₃/BiVO₄ interfaces models

The WO₃ (001) slabs have been interfaced with the three BiVO₄ (010) models described above. All composite models have been fully optimized. The calculated lattice parameters are reported in Table S4, together with the calculated adhesion energy Eₐₐ, defined as:

\[ E_{ad} = E_{WO₃/BiVO₄} - (E_{WO₃(001)} + E_{BiVO₄(010)}) \]

Table S4. Optimized lattice parameters (a, b, γ), surface area (A) and adhesion energy (Eₐₐ) of the heterojunction models with increasing BiVO₄ thickness.

| WO₃/BiVO₄ thickness / nm | a / Å  | b / Å  | γ / degrees | A / Å² | Eₐₐ / J m⁻² |
|--------------------------|--------|--------|-------------|--------|-------------|
| 2.7                      | 7.276  | 7.292  | 92.0        | 53.0   | -0.12       |
| 3.8                      | 7.267  | 7.267  | 91.8        | 52.8   | -0.13       |
| 5.0                      | 7.262  | 7.255  | 91.7        | 52.7   | -0.13       |
d. Band Alignment of WO$_3$/BiVO$_4$ interfaces models

The valence band ($VBM_{WO_3}$, $VBM_{BiVO_4}$) and conduction band ($CBM_{WO_3}$, $CBM_{BiVO_4}$) edges of independent components can be aligned by using, as a common reference, the calculated plane averaged electrostatic potential ($V$) along the non-periodic dimension $z$. In particular, the stationary points of $V$ ($V^{TOP}$) in the interplanar regions of each isolated unit ($V^{TOP}_{WO_3}$, $V^{TOP}_{BiVO_4}$) are compared to those of the interface ($V^{TOP}_{WO_3,Het}$, $V^{TOP}_{BiVO_4,Het}$). In this way, the band structures are aligned to a common reference energy, permitting to evaluate the shift induced by the interfacial effects. The valence band offset ($VBO$) and conduction band offset ($CBO$) can hence be calculated as:

$$VBO = (VBM_{WO_3} - V^{TOP}_{WO_3}) - (VBM_{BiVO_4} - V^{TOP}_{BiVO_4}) + (V^{TOP}_{WO_3,Het} - V^{TOP}_{BiVO_4,Het})$$

$$CBO = (CBM_{WO_3} - V^{TOP}_{WO_3}) - (CBM_{BiVO_4} - V^{TOP}_{BiVO_4}) + (V^{TOP}_{WO_3,Het} - V^{TOP}_{BiVO_4,Het})$$

Table S5. Calculated $VBO$ and $CBO$ of WO$_3$/BiVO$_4$ interfaces based of separated units and explicit interface calculations. The minus sign indicates that WO$_3$ band edges are lower in energy that the same of BiVO$_4$.

| WO$_3$/BiVO$_4$ thickness / nm | separated | interface |
|-------------------------------|-----------|-----------|
|                               | VBO / eV  | CBO / eV  | VBO / eV  | CBO / eV  |
| 5.0                           | -0.9      | -1.31     | -1.22     | -1.69     |

The formation of the interface leads to a ~0.3 eV enhancement of the band offsets, which is expected to improve the driving force of the electrons migration toward WO$_3$ and holes migration towards BiVO$_4$. This 0.3 eV band offsets increase is similar to what obtained in oxide interfaces.$^5$

References

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