

Assessing capability of semiconductors to split

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that quantitatively accurate surface dependent IPs and EAs can be computed by correcting density functional theory with accurate many-body GW calculations. Second, by comparing positions of the band edges of the same materials derived from IPs and EAs with those measured electrochemically and expressed at the pH value corresponding to the point of zero charge (PZC), we find that there is on average a 0.5 eV shift of the calculated band edges closer to the vacuum due to the interaction with water molecules at the interface. This result allows direct alignment of the semiconductor band edges with water redox potential just on the basis of known IPs and EAs eliminating explicit calculations of semiconductor/water interfaces. In this way an efficient, reliable and computationally relatively simple procedure can be constructed and used in searching for new water splitting materials.

Our computational approach includes accurate many-body GW calculations for the electronic structure of bulk materials in combination with density functional theory (DFT) calculations of the corresponding surface (slab) systems for the purpose of obtaining the absolute (vacuum) reference energy, resulting in accurate, and surface orientation dependent, IPs and EAs of semiconductors and insulators. The power of this approach is in its broad applicability across the periodic table, which is enabled by employing recent developments that allow application of the GW calculations to transition metal compounds²⁶ which are known to be rather challenging for the ab initio based methods.

introduce electrons or holes into the conduction or the valence band, thereby allowing the Δ

shown in Fig. 4. The VMB and CBM of SrO terminated SrTiO₃(001) surfaces are calculated to be by 2.3 eV closer to the vacuum than the IP and EA of the TiO₂ terminated surface. This is not surprising as the differences between the calculated values for pure TiO₂, both rutile (IP = 7.51, EA = 4.67) and anatase (IP = 7.82 eV, EA = 4.62), and estimated ones for SrO (EA = 0.64 eV⁴⁹)[‡] are of the same magnitude. It is frequently observed in experiments that SrO termination appears to be in relatively small fraction, i.e. as terraces, on mostly TiO₂ terminated (001) surfaces.^{50,51} However, our calculated IPs and

i.e. those reported in ref. 8. Just by comparing the calculated

and Cu_2O . Predicted VBM and CBM positions are closer to the vacuum than the measured ones by 1.2 and 1.8 eV, respectively, and this difference cannot be explained by their PZC values.

To estimate the magnitude of the Δ_{dipole} we compare VBM and CBM positions derived from the calculated IPs and EAs, with those measured electrochemically, but now expressed using the Nernst equation, at the $\text{pH} = \text{PZC}$ of the corresponding material. The comparison is presented in Table 1 for the VBMs of all materials considered in this work for which the PZC values are available in the literature.^{9,65,66} Analogous results can be obtained for the CBM positions. The reality is that the reported PZC values can span a pretty large range of values, depending both on the measurement technique and the method used to grow the material.⁶⁶ For example, in the case of rutile TiO_2 it is possible to find PZC values ranging from 3.4 to about 7.0 in ref. 66, which contains a collection of measured PZC for many different materials coming from different sources. In Table 1 we use average PZC from ref. 66 and the values reported in ref. 9, 65 and 67. The last column in Table 1 lists the differences of the experimental VBM positions at $\text{pH} = \text{PZC}$ and the VBMs derived from the calculated IPs. Relatively wide ranges of values reflect both the spread in PZC and the spread in the reported VBM positions at $\text{pH} = 1$.

Interestingly, all the differences are positive and average of around 0.5 eV (± 0.3 eV). Since $\text{VBM}^{\text{exp.}} - \text{VBM}^{\text{theory}}$

electrochemically and provides insight into details of the material/water interface, and that, even without this shift, the search for new water splitting materials can be guided solely using IPs and EAs.

4 Conclusions

In conclusion, we demonstrate on a set of 17 materials: (i) that direct DFT calculations of IPs and EAs of semiconductors and insulators can be corrected by the bulk GW band-edge shifts resulting in quantitative IPs and EAs, (ii) from the extensive comparison of calculated IPs and EAs with available experimental data, both from photoemission and electrochemical measurements, we show that it is possible to sort candidate water splitting materials solely from IPs and EAs, and (iii) that the effect of an aqueous environment can be approximated at $\text{pH} = \text{PZC}$ by the 0.5 eV up shift of both VBM and CBM closer to the vacuum thereby eliminating the need for explicit calculations of material/water interfaces. These results allow alignment of the semiconductor electronic bands with water reduction and oxidation potentials just on the basis of known (measured or calculated) IPs and EAs and direct assessment of the potential of semiconductors to split water.

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