

Electron and Hole Polarons at the BiVO₄–Water Interface

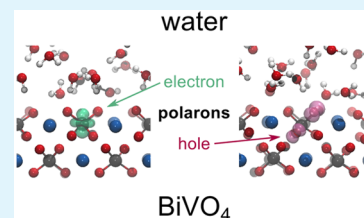
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S Supporting Information

ABSTRACT: We determine the transition levels of electron and hole polarons at the BiVO₄–water interface through thermodynamic integration within a hybrid functional scheme, thereby accounting for the liquid nature of the water component. The electron polaron is found to be less stable at the interface than in the bulk by 0.18 eV, while for the hole polaron the binding energy increases by 0.20 eV when the charge localizes in the surface layer of BiVO₄. These results indicate that interfacial effects on the polaron binding energy and charge distribution are sizeable and cannot trivially be inferred from bulk calculations.

KEYWORDS: water splitting, bismuth vanadate, polarons, DFT, molecular dynamics



1. INTRODUCTION

Photocatalytic water splitting is a promising technique to transform solar energy into fuel in the form of hydrogen. In a water-splitting cell, photogenerated electrons and holes originating from a photoabsorber drive H⁺ reduction and H₂O oxidation. These reactions occur at the semiconductor–water interface; therefore, their efficiency is affected by the processes occurring at the interface.

Bismuth vanadate has emerged as a promising photoanode for water-splitting photoelectrochemical cells^{1–4} due to its band gap allowing for the absorption of a substantial portion of the visible light and the favorable position of the band edges with respect to the water redox potentials. The bulk properties of BiVO₄ have been the subject of numerous computational studies.^{5–8} However, since the water-splitting reaction occurs at the interface with water, the material surface and the presence of the solvent strongly impact the relevant phenomenon. It has previously been shown that the electron and hole in bulk BiVO₄ localize forming polarons.⁹ These states introduce transition levels within the band gap and thus affect the band alignment with the water redox levels. However, it can be expected that the polaronic levels in the bulk and at the interface differ, for example, due to the occurrence of broken bonds in the latter case.

In this Letter, we study hole and electron polarons at the interface between BiVO₄ and water through the use of an atomistic interface model that accounts for the thermal motion of the water molecules. The molecular dynamics (MD) simulations are carried out at the hybrid functional level to properly describe the localization of excess holes and electrons at the interface. The polaron binding energies are then consistently determined through the thermodynamic integration method within the same theoretical scheme. Our work reveals the energy levels and charge localization of interfacial electron and hole polarons in comparison with their bulk counterparts.

2. METHODS

To study polarons at the BiVO₄–water interface, we perform molecular dynamics simulations using the hybrid functional PBE0,¹⁰ which allows one to treat the self-interaction error^{11–13} and to describe localized electronic states.¹⁴ In the PBE0 functional, we set the mixing parameter α to 0.22. After taking into account various corrections affecting the electronic structure of BiVO₄, such as spin–orbit coupling, thermal, and quantum effects, such a functional reproduces well the experimental band gap of approximately 2.6 eV.⁸ This choice is based on the fact that a hybrid functional reproducing the correct band gap of a semiconductor is also capable of describing polaronic distortions, as shown by Miceli et al.¹⁴ We describe van der Waals (vdW) interactions through the nonlocal rVV10 functional.¹⁵ The empirical parameter b of the rVV10 functional is set to 7.7 to reproduce the experimental density of water for the employed hybrid functional. This value is based on the interpolation of results from refs 16 and 17, where the optimal b parameter was determined for $\alpha = 0$ and $\alpha = 0.40$. The MD simulations are performed with the CP2K code¹⁸ in the canonical NVT ensemble at a temperature of 350 K. This temperature is chosen to achieve a frank diffusive motion of water. We note that this temperature differs from the one used in our previous study on bulk polarons in BiVO₄ (300 K).⁹ However, by linearly extrapolating the temperature effect on the bulk polarons found in the previous study from 300 to 350 K, we find that the results at these two temperatures coincide within 35 meV. Therefore, the results on the interface polarons presented in this work can be compared with the levels calculated in the bulk. We use atom-centered Gaussian-type functions to describe the atomic orbitals and an auxiliary plane wave basis set to re-expand the electron density. For Bi, O, and V, we employ double- ζ MOLOPT basis sets.¹⁹ For H, a triple- ζ basis set is employed. The cutoff energy is set to 600 Ha for the plane waves. Core–valence interactions are described by Goedecker–Teter–Hutter pseudopotentials.²⁰

We model the BiVO₄(010)–water interface with an orthorhombic supercell ($a = 10.39$ Å, $b = 10.18$ Å, and $c = 36.17$ Å) containing a six-layer semiconductor slab and 56 water molecules. We approximate

Received: February 26, 2019

Accepted: April 25, 2019

Published: April 25, 2019

the β angle of the $C2/c$ monoclinic structure to 90° . The employed slab is symmetric; therefore, the two interfaces are equivalent. A representative configuration of the studied system is given in Figure S1. The MD is initiated with equilibrated configurations taken from previous simulations of the considered system.^{21,22} We sample the Brillouin zone at the Γ point. The simulations are evolved for about 5 ps using a time step of 0.5 fs. The hole and electron polarons are generated by adding a single positive or negative charge to the simulation cell. In these cases, we perform calculations including spin-polarization. We introduce initial distortions in the first layer of the BiVO_4 slab to avoid polaron formation in the bulk region. We use the results of ref 8 to account for the effects of finer k -point sampling and spin-orbit coupling on band edge positions, as they cannot be directly included in the present calculations within the CP2K code. Finite-size corrections^{23–25} to the energy levels of the polarons are neglected, considering the large dielectric constants of water ($\epsilon_0 = 78.3$)²⁷ and BiVO_4 ($\epsilon_0 = 68$).²⁶ We calculate the energy levels of the localized holes and electrons at the BiVO_4 –water interface through the thermodynamic integration (TI)²⁸ method. Further details on the TI calculations of the transition levels can be found in the Supporting Information. We note that in the case of hole and electron polarons, the binding energies E_b (energies of localized charges relative to those of free states) can be directly related to the transition levels μ . For the electron, this relationship reads $E_b^{\text{el}} = \epsilon_c - \mu_{\text{el}}$ and for the hole, $E_b^{\text{h}} = \mu_{\text{h}} - \epsilon_v$, where ϵ_c and ϵ_v are the positions of the conduction and valence band edges, respectively.

3. RESULTS AND DISCUSSION

We first analyze the results for the electron polaron. A representative instantaneous isodensity of the electron polaron at the interface is shown in Figure 1. We compare the interface

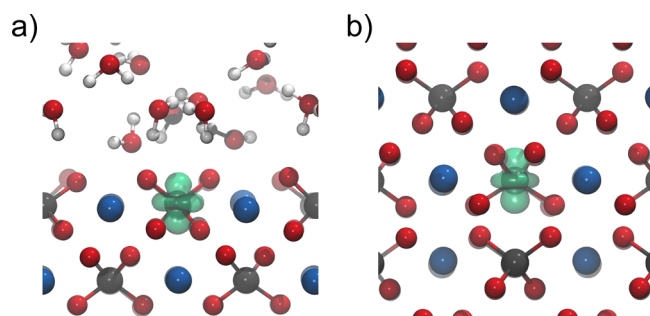


Figure 1. Isodensities of the electron polaron (a) at the BiVO_4 –water interface and (b) in bulk BiVO_4 .

polaron with its bulk counterpart.⁹ The same distribution of localized charge can be noticed in the two cases. The electron localizes at a single V atom, changing its ionization state from +5 to +4 through the occupation of an empty 3d orbital. The d orbital shape can be clearly recognized in Figure 1. Through thermodynamic integration, we find the transition level associated with the electron polaron to lie 0.70 eV below the conduction band minimum of BiVO_4 . In Figure 2, we align the transition level of the electron polaron at the interface with respect to its bulk level, the BiVO_4 band edges, and water redox levels. We use data from ref 9 to plot the alignment of these levels for pH = 7. In ref 9, a binding energy of 0.88 eV was found for the bulk polaron. This means that the binding energy related to the electron polaron at the interface is 0.18 eV lower than in the bulk.

To understand the lower binding energy of the electron polaron at the interface, we analyze the geometry of the VO_4 unit in which the charge is localized. We show in Figure 3 the vanadium–oxygen radial distribution function $g_{\text{V-O}}(r)$ for the

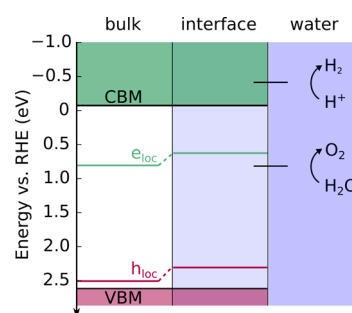


Figure 2. Alignment of the polaron transition levels in bulk BiVO_4 and at the interface with the H^+/H_2 and $\text{O}_2/\text{H}_2\text{O}$ redox levels at pH = 7.

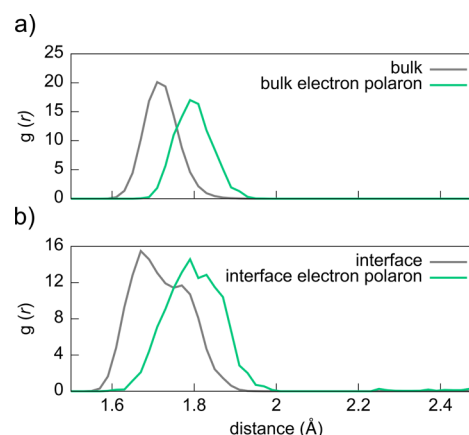


Figure 3. V–O radial distribution functions in (a) bulk BiVO_4 and (b) at the BiVO_4 –water interface with and without the electron polaron.

cases of charged and neutral VO_4 units in the bulk and at the interface. First, one notices that the trapping of an electron leads to the expansion of the V–O bonds both in the bulk and at the interface. Second, we observe a distribution with a single peak in the bulk and one with a double peak at the interface, both in the presence and in the absence of polaron trapping. This means that the VO_4 unit is asymmetrically distorted at the interface with the V–O bonds oriented toward the surface, being shorter than those oriented toward the bulk. The larger delocalization of the polaron associated with this symmetry breaking provides an explanation for the lower stability of the polaron at the interface. We also investigate the effect of the water molecules on the electron polaron at the interface by examining a randomly chosen configuration. The calculation is described in the Supporting Information. We find that in the absence of water, the electron polaron is even less stable at the surface (the binding energy is lower by approximately 0.4 eV as compared with the bulk) and that the water molecules stabilize the localized charge by approximately 0.2 eV. We note that the lower stability of the electron polaron at the surface was also noticed in a recent study of Mo-doped and W-doped BiVO_4 .²⁹

Next, we focus on the hole polaron at the interface. In Figure 4, the isodensity of an instantaneous configuration of the hole polaron at the BiVO_4 surface is shown and compared with the typical one of the bulk.⁹ Unlike for the electron polaron, the distribution of localized charge of the hole strongly differs between the bulk and the interface. In the bulk, the charge is localized within a BiO_8 unit. At the surface, the hole is mostly shared among two oxygen atoms neighboring an interfacial

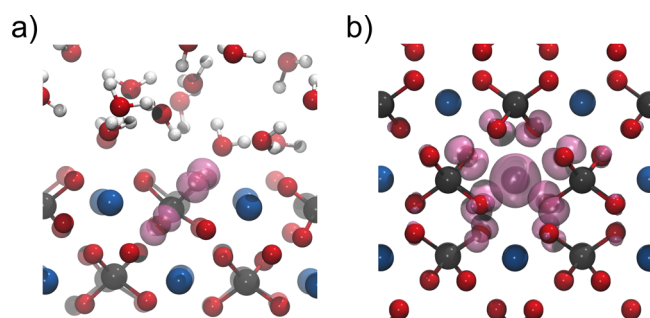


Figure 4. Isodensities of the hole polaron (a) at the BiVO_4 –water interface and (b) in bulk BiVO_4 .

vanadium atom. Due to the charge localization, the distance between the two O atoms reduces to 2.29 Å on average, compared to the value of 2.78 Å observed between oxygen pairs in units of VO_4 at the interface. We attribute the different localization of the hole at the interface and in the bulk to the fact that a formation of a bond between two oxygen atoms is energetically more favorable than partial localization on eight atoms. In the bulk, however, interactions with other atoms keep the two oxygen atoms apart and prevent the formation of such a bond, while at the interface, one of the oxygen atoms can move more freely. We note that in the presence of higher carrier concentrations, the formation of a double bond between the two oxygen atoms (O_2^- anion) could even lead to further charge stabilization. From the radial distribution function in Figure 5, one notices no significant change in the

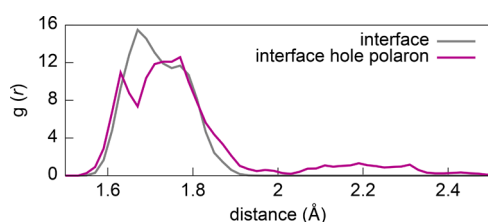


Figure 5. V–O radial distribution functions at the BiVO_4 –water interface with and without the hole polaron.

V–O bond lengths within the VO_4 unit. However, a second feature around 2.3 Å is observed in the $g_{\text{V-O}}(r)$. This peak corresponds to a displacement of one oxygen atom belonging to a VO_4 unit in the second layer toward the localized charge.

The stronger polaron localization of the hole polaron at the interface leads to a higher binding energy compared to the bulk case. Through thermodynamic integration, we find that the transition level associated with the localized hole at the interface lies at 0.31 eV from the valence band maximum, to be compared with the binding energy of 0.11 eV found in the bulk.⁹ The energy levels of the hole polaron have been included in Figure 2.

Our results have implications for the modeling of materials in water-splitting devices as well as for ongoing search for materials. First, we have shown that the energetics of the polaronic states at the interface and in the bulk differ significantly. This means that the alignment of the energy levels at the BiVO_4 –water interface cannot trivially be inferred from bulk calculations. Second, for the hole polaron, we notice that its charge distribution undergoes significant change at the surface of the semiconductor. Therefore, bulk models of polarons in complex oxides might not even give qualitative

insight into the charge localization occurring at the interface. This highlights the importance of modeling the interface explicitly for understanding the redox processes in water-splitting cells, which is a fundamental aspect in the search for new photoanode materials. Finally, our results show that the hole is most stable at the surface of BiVO_4 , while the electron preferentially localizes deeper in the bulk. This spatial separation between electron and holes is expected to reduce the recombination rate between photogenerated charges and could lie at the origin of the high photocatalytic performance of bismuth vanadate.³⁰

4. CONCLUSIONS

In conclusion, we analyze the role of the BiVO_4 –water interface in the localization of excess charges. We combine hybrid functional molecular dynamics with thermodynamic integration to calculate the transition levels related to the hole and electron polarons at the interface. We find that the binding energy of the interfacial electron polaron amounts to 0.70 eV, lower than the bulk value of 0.88 eV. We attribute the electron polaron destabilization to the lower localization induced by the distorted VO_4 units at the interface. For the hole polaron, we show that the charge distribution undergoes significant change at the interface. While the hole localizes within a BiO_8 unit in the bulk, the charge density is mostly shared among only two oxygen atoms at the interface. The stronger localization at the interface leads to a deeper transition level at 0.31 eV above the valence band maximum. Our results highlight the importance of accounting for interfacial effects when addressing the localization and energetics of excess charges in complex oxides.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b03566.

Details concerning the simulation cell, methods used to calculate the polaron transition levels within the thermodynamic integration method, and tests on the effect of water on the interface polarons (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Francesco Ambrosio for the models of the BiVO_4 –water interface. The authors acknowledge financial support from the Swiss National Science Foundation (SNSF) (grant no. 200020-172524). This work has been realized in relation to the National Center of Competence in Research (NCCR) “Materials’ Revolution: Computational Design and Discovery of Novel Materials (MARVEL)” of the SNSF. We used computational resources of CSCS and SCITAS-EPFL.

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