Supporting Information for publication

First-principles investigation of electronic properties of Bi_2O_4 (101)/BiVO₄ (010) heterojunction towards more efficient solar water splitting[†]

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Section 1:



Fig. S1 different k-point for model A are used to evaluate the accuracy of the calculation.

We chose $1 \times 1 \times 1, 3 \times 1 \times 1, 4 \times 2 \times 1$ and $5 \times 3 \times 1$ supercells to compare the difference of binding energy in Fig. S1. As shown, the difference of binging energy between different supercell are very small. So we select $3 \times 1 \times 1$ supercell for the calculations.

	Crystallographic parameters			Atomic fractional coordinates				Bond length		
	$A(\text{\AA})$	$b(\text{\AA})$	<i>c</i> (Å)	$\beta(^{\circ})$	Bi	V	O ₁	O ₂	Bi-O/ Å	V-O/ Å
This work	7.30	11.7	5.19	135	(0,0.61	(0,0.120	(0.242,	(0.131,	2.417×2	1.737×2
	01	044	56	.75	6,0.25)	,0.250)	0.458,	0.199,	2.440×2	1.746×2
				6			0.343)	0.142)	2.459×2	
									2.522×2	
Power	7.25	11.7	5.08	134	(0,0.13	(0,0.361	(0.263,	(0.349,	2.314×2	1.740×2
neutron	8	06	4	.07	6,0.25)	,0.25)	0.052,	0.210,	2.349×2	1.752×2
diffractio				3			0.382)	0.858)	2.533×2	
n (4.5K) ^{S1}									2.676×2	

Table S1. Optimized crystallographic parameters of ms-BiVO₄ compared to experimental data. The atomic fractional coordinates of all atoms and the bond lengths are also presented.

Power	7.24	11.6	5.09	134	(0,0.13	(0,0.370	(0.261,	(0.354,	2.354×2	1.691×2
neutron	7	97	0	.22	4,0.75)	,0.25)	0.051,	0.208,	2.372×2	1.772×2
diffractio				6			0.380)	0.861)	2.516×2	
n (295K) ^{s2}									2.628×2	
Powder	7.29	11.6	5.19	135	(0,0.61	(0,0.119	(0.238,	(0.112,	2.307×2	1.562×2
X-ray	63	972	35	.76	59,0.2	,0.25)	0.461,	0.196,	2.385×2	1.785×2
diffractio				7	5)		0.345)	0.114)	2.640×2	
n (295K) ^{S3}									2.703×2	

Table S2. Lattice parameters of $BiVO_4(010)$ and all low-index Bi_2O_4 surfaces, the lattice mismatch for possible heterojunction formation is also presented.

	*	e		
	a/Å	b/Å	$ heta_{/^{\circ}}$	ΜΑΧ δ
BiVO ₄ (010)	5.196	5.094	90	
Bi ₂ O ₄ (001) A	6.692	5.118	112.482	
Bi ₂ O ₄ (00 ¹) B	5.118	6.692	112.482	
Bi ₂ O ₄ (100) A	5.118	5.567	90	0.093
Bi ₂ O ₄ (100) B	5.567	5.118	90	0.071
Bi ₂ O ₄ (010) A	5.567	11.906	81.409	
Bi ₂ O ₄ (010) B	11.906	5.567	81.409	
Bi ₂ O ₄ (110) A	5.567	6.692	106.442	
Bi ₂ O ₄ (110) B	6.692	5.567	106.442	
Bi ₂ O ₄ (101) A	15.037	5.118	90	0.037
Bi ₂ O ₄ (101) B	5.118	15.037	90	0.016
$\operatorname{Bi_2O_4}(\overline{10}_1) \operatorname{A}$	5.118	11.906	90	0.169
$Bi_2O_4(\overline{10}_1)B$	11.906	5.118	90	0.146
$\operatorname{Bi_2O_4(01\overline{1})A}$	12.367	7.562	103.033	
$Bi_2O_4(01\overline{1}) B$	7.562	12.367	103.033	
Bi ₂ O ₄ (011) A	12.367	7.562	76.967	
Bi ₂ O ₄ (011) B	7.562	12.367	76.967	
Bi ₂ O ₄ (111) A	6.692	7.562	92.891	
Bi ₂ O ₄ (111) B	7.562	6.692	92.891	
$Bi_2O_4(11\overline{1}) A$	6.692	7.395	64.709	
$Bi_2O_4(11\overline{1}) B$	7.395	6.692	64.709	
$\operatorname{Bi}_2\operatorname{O}_4(1\overline{1}1)\operatorname{A}$	6.692	7.562	87.109	
$\operatorname{Bi}_2\operatorname{O}_4(1\overline{1}1)\operatorname{B}$	7.562	6.692	87.109	

In the table, we use θ to represent the value of crystal axis angles α and γ (for monoclinic crystal, $\alpha = \gamma = 90^{\circ}$). The different low-index surface can match with BiVO₄(010) when $\theta = \alpha = \gamma = 90^{\circ}$. Accordingly, Bi₂O₄(100), Bi₂O₄(101), Bi₂O₄(101) surfaces are selected to match with BiVO₄(010) surface, and we can rotate surface A 90° to get surface B. Furthermore, the

lattice mismatch of BiVO₄ (010) and selected Bi_2O_4 surfaces were calculated, the maximum value (MAX δ) on two sides was chosen as the lattice mismatch of each interface.



Fig. S2 The overall surfaces considered in this paper, where the same surfaces are put together. Based on the symmetry of ms-Bi₂O₄, the following planes are equivalent: (001) and ($\overline{001}$); (100) and ($\overline{100}$); (010) and ($\overline{010}$); (110), ($\overline{110}$), ($\overline{110}$) and ($\overline{110}$); (101) and ($\overline{101}$); ($\overline{101}$) and (10) $\overline{1}$); ($\overline{011}$) and ($\overline{011}$); (011) and ($\overline{011}$); (111) and ($\overline{111}$); ($\overline{111}$), ($\overline{111}$), ($\overline{111}$) and ($\overline{111}$); ($\overline{111}$) and ($\overline{111}$). Therefore, we only selected the (001), (100), (010), (110), (101), ($\overline{101}$), ($\overline{011}$), (011), (111), ($\overline{111}$) and ($\overline{111}$) surface during calculation.



Fig. S3 Two types of interface models of $Bi_2O_4/BiVO_4$ heterojunction, we can rotate Bi_2O_4 90° around Z-axis and keep $BiVO_4$ the same to obtain another interface model.



Fig. S4 Surface structure and lattice parameters of BiVO₄(010) and selected Bi₂O₄ surfaces. Bi (purple), V (gray), and O (red) atoms are shown in colored spheres. BiVO₄(010) (1×1) matches well with Bi₂O₄(100) A and B, while BiVO₄(010) (3×1) matches with Bi₂O₄(101) A and Bi₂O₄ ($\overline{1}$ 01) A surface. Meanwhile, BiVO₄(010) (1×3) matches with Bi₂O₄(101) B and Bi₂O₄ ($\overline{1}$ 01) B surfaces, where (3×1) and (1×3) represent the BiVO₄(010) are triple size along a direction and b direction. The difference between surface A and B are the lattice parameters of a and b interchanged, which means facet B can be obtained by rotating facet A 90° around Z axis. In this way, there are two different types of interfaces when each Bi₂O₄ surface is laid on top of BiVO₄(010).



Fig. S5 (a) The binding energy of two Bi_2O_4 (101)/BiVO_4 (010) interfaces with different distance. (b) The green dashed section are selected interface layer of model A (on the top) and model B (on the bottom), which are choose to calculate the PDOS. Bi (purple), V (gray), and O (red) atoms are shown in colored spheres.





Fig. S6 (a) The geometric structure and electron density difference map of Bi_2O_4 (101)_B/BiVO_4 (010) interface model, a loss of electrons is indicated in blue, while electron enrichment is indicated in red; (b) the PDOS of Bi_2O_4 (101)_B/BiVO_4 (010) interface, where scissors operation for BiVO_4 (0.35 eV) and Bi_2O_4 (1.02 eV) are used to overcome the intrinsic underestimation of band gap by DFT.



Fig. S7 (a), (b) and (c) show work function of $BiVO_4(010)$, $Bi_2O_4(101)_A$ and $Bi_2O_4(101)_B$ single layer, respectively. (d) The corresponding partial density of states (PDOS) of Bi_2O_4 $(101)_A$, $Bi_2O_4(101)_B$ and $BiVO_4(010)$. We calculate the work functions of $BiVO_4(010)$ and two types $Bi_2O_4(101)$ surface, as shown in Figure S4 (a), (b) and (c). The work functions of $BiVO_4(010)$, $Bi_2O_4(101)_A$ and $Bi_2O_4(101)_B$ surface is 6.89 eV, 6.11 eV and 6.05 eV, respectively. Figure S4 (d) shows that the calculated value of band gap for $Bi_2O_4(101)_A$, $Bi_2O_4(101)_B$ and $BiVO_4(010)$ is 2.0 eV, 2.0 eV and 2.4 eV. During the calculation, scissors operation was used to obtain more accurate result due to the underestimation of band gap typical of DFT.^{S4,S5}



Fig. S8 Schematic diagram of the possible charge separation for model B during photocatalysis.



Fig. S9 Different Bi sites on $BiVO_4$ and Bi_2O_4 surfaces. There is only one kind of Bi site on $BiVO_4$ surface, whereas there are two kinds of Bi sites on Bi_2O_4 surface. Bi (purple), V (gray), and O (red) atoms are shown in colored spheres.

Section 2:

The adsorption on $BiVO_4$ surface plays an important role in PEC water oxidation reaction. The oxidation evolution reaction (OER) occurs at the anode at the standard oxidation potential of 1.23 V (*vs.* NHE). ORE is a four-electron-transfer process, the minimum free energy required to split two molecules of water under equilibrium and standard conditions is estimated by:

$$\Delta G_{0_2} = 4 \times 1.23 = 4.92 \ eV \tag{1}$$

The NHE potential is defined as the following half reaction

$$H_{2(g)} \leftrightarrow H_{sol}^{+} + e_M \tag{2}$$

If the NHE potential is set at zero, we will obtain

$$\mu_{H^{+}} + \mu_{esur} = \frac{1}{2}\mu_{H_2}$$

With the process of a single electron transfer, water splitting can be divided into four reaction paths, as shown in R1 to R4^{S6,S7}

$$R1: {}^{H_2O} + * \leftrightarrow OH^* + H^+ + e^-$$
(3)

$$R2: \theta H^* \leftrightarrow \theta^* + H^+ + e^- \tag{4}$$

R3:
$${}^{0^*} + H_2 0 \leftrightarrow 00H^* + H^+ + e^-$$
 (5)

$$R4: {}^{OOH}{}^* \leftrightarrow O_2 + H^+ + e^- \tag{6}$$

1

where * represents a surface site. The free energy of each adsorbate can be calculated as:

$$\Delta G_{OH} = E_{OH^*}^{DFT} - E_{surface} - \mu_{H_2O}^{\theta} + \frac{1}{2}\mu_{H_2}^{\theta} - \hat{G}_{OH^*}$$

$$A G_{OH} = E_{OH^*}^{DFT} - E_{surface} - \mu_{H_2O}^{\theta} + \frac{1}{2}\mu_{H_2}^{\theta} - \hat{G}_{OH^*}$$
(7)

$$\Delta G_{OOH} = E_{OOH^*}^{DFT} - E_{surface} - 2\mu_{H_2O}^{\theta} + 1.5\mu_{H_2}^{\theta} - G_{OOH^*}$$
(9)

where \hat{G}_i includes contributions from the vibrational energy(ZPE and internal energy) and entropy of the adsorbate at 300K. This correction is calculated using the harmonic approximation for every adsorbate and surface studied, with typical values of 0.35, 0.05, and 0.40 for OH*, O*, and OOH*, respectively. The following equations summarize the shift of standard free energy during each elementary step

$$\Delta G_{R1}^{\,\nu} = \Delta G_{OH} \tag{10}$$

$$\Delta G_{R2}^{\theta} = \Delta G_0 - \Delta G_{0H} \tag{11}$$

$$\Delta G_{R3}^{\theta} = \Delta G_{00H} - \Delta G_0 \tag{12}$$

$$\Delta G_{R4}^{\theta} = \Delta G_{02}^{\theta}(g) - \Delta G_{00H}$$
⁽¹³⁾

On the basis of the equilibrium condition $\sum_{j} v_{j} u_{j} = 0$, we can obtain the surface potential relative to the solution if the NHE potential is considered to be zero.

$$\eta_{sur} - \eta_{sol} = \Delta G_{Ri}^{\theta} / e \tag{14}$$

As a result, the theoretical overpotential obtained from the Gibbs free energy difference at each step can be expressed as:

$$\eta = \frac{\max\left(\Delta G_{Ri}^{\theta}\right)}{e} - 1.23 \tag{15}$$

This means that the overpotential is zero if $\Delta G_{R1}^{\theta} = \Delta G_{R2}^{\theta} = \Delta G_{R3}^{\theta} = \Delta G_{R4=1.23}^{\theta}$ eV, and this would define the ideal catalyst.

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