Charge transport, interfacial interactions and synergistic mechanism in $BiNbO_4/MWO_4$ (M = Zn and Cd) heterostructures for hydrogen production: insights from a DFT + *U* study

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Introduction

- Strong dependence on the low-efficient power generation from non-renewable fossil fuels produces a significant quantity of carbon dioxide, which induces a greenhouse effect [1].

- Photocatalysis, which directly converts clean and abundant solar energy to solar fuels, and chemical energy is considered as a promising technique among the several alternative energy approaches [2].

- Thermodynamically, the photocatalyst should have
  - ✓ enough band gap energy
  - ✓ suitable band edge positions
  - ✓ high charge carrier mobility
  - ✓ high stability and activity

[1] X. Zou and Y. Zhang, Chem. Soc. Rev., 2015, 44, 5148-5180
[2] M.-Q. Yang, N. Zhang, M. Pagliaro and Y.-J. Xu, Chem. Soc. Rev., 2014, 43, 8240-8254.

Introduction cont'd

- Metal tungstates, such as $CdWO_4$ and $ZnWO_4$ are a significant family of inorganic materials that have received much attention in photocatalysts [3,4]
  - ✓ excellent catalytic activity
  - ✓ high chemical stability
  - ✓ low-cost
  - ✓ commercial availability

- Draw back
  - ✓ wider bandgap energy
  - ✓ low quantum yield

- Solution
  - ✓ electronic coupling of semiconductors with different bandgaps

[3] P. Li, X. Zhao, Y. Li, H. Sun, L. Sun, X. Cheng, X. Hao and W. Fan, CrystEngComm, 2012, 14, 920-928

Objectives

- To investigate the structural, charge carriers mobility and separation, optical and electronic properties of these hybrid heterostructures and the pure systems.

- To understand the origin of the enhanced photocatalytic activity of the hybrid heterostructures.

- To test the suitability of the proposed heterostructures towards water splitting application.

Computational Details

- Software
  - ✓ Cambridge Serial Total Energy Package (CASTEP) - Materials Studio 2016 [4].

- Hardware
  - ✓ Clusters from the Centre for High Performance Computing (CHPC), Cape Town.
  - ✓ Computational Laboratory, Department of Applied Chemistry, UJ.

[4] Accelrys Materials Studio 2016. Accelrys Inc., 5005 Wateridge Vista Drive, San Diego, CA 92121 USA (2014).

Computational Details cont'd

Molecules Building - Material Studio GUI

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Geometry Optimization
[Generalized Gradient approximation (GGA) functional of the Perdew-Burke-Ernzerhof (PBE) scheme and ultrasoft psedopotential]

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Electronic property calculation
[GGA+*U* method]

Computational Details cont'd

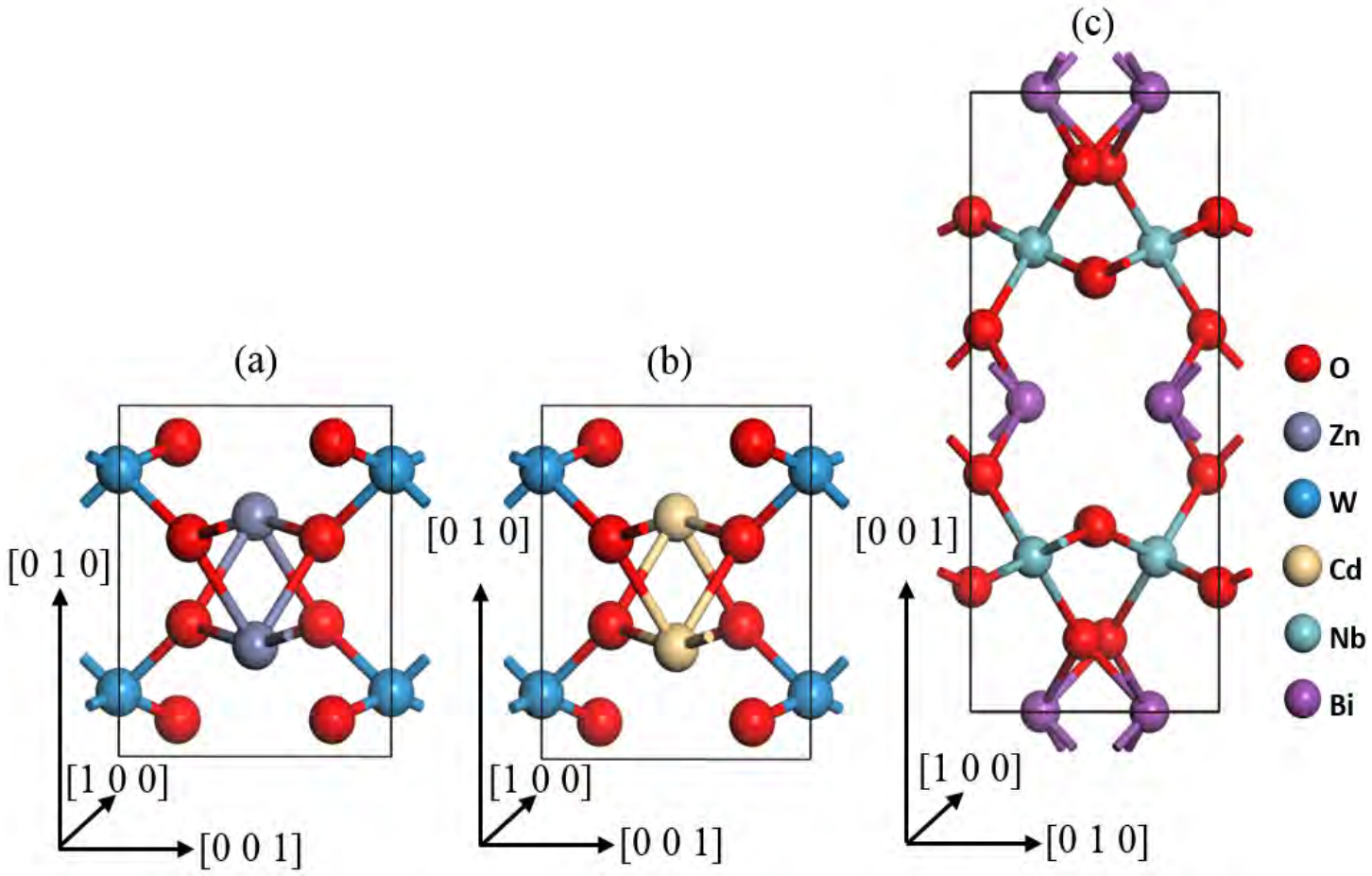

Figure 1. The crystal structures of (a) $ZnWO_4$, (b) $CdWO_4$ and (c) $BiNbO_4$ with several low–index planes indicated by arrows.

Results and Discussion

Table 1. The surface energy (J m^{-2}) of (100), (010) and (001) slabs for $ZnWO_4$, $CdWO_4$ and $BiNbO_4$.

Species	(100)	(010)	(001)
$ZnWO_4$	0.943	0.349	0.524
$CdWO_4$	1.084	0.098	0.203
$BiNbO_4$	1.670	0.680	0.990

$$\gamma = \frac{E_{slab} - E_{bulk}}{2A} \qquad (1)$$

where E_{slab} and E_{bulk} are the total energy of the bulk units and the relaxed slab, respectively. *A* is the surface area of the slab

Results and Discussion cont'd

Table 2. Calculated and experimental band gap (eV), equilibrium lattice constants (Å) and average M–O bond lengths (Å) for bulk $BiNbO_4$, $CdWO_4$ and $ZnWO_4$.

	Band gap			Lattice parameters								
				Calculated				Experimental				
	GGA	GGA+U	Exp.	a	b	c	γ	a	b	c	γ	*$D_{M–O}$
$ZnWO_4$	2.90	3.75	3.75	4.671	5.714	4.928	90.46	4.693	5.721	4.928	90.63	2.12
$CdWO_4$	2.98	3.80	3.80	5.011	5.050	5.826	91.41	5.013	5.090	5.866	91.50	2.43
$BiNbO_4$	3.15	3.48	3.50	5.682	11.716	4.984	90.00	5.679	11.708	4.982	90.00	2.02

*The $D_{M–O}$ is the average bond lengths of Zn–O, Cd–O and Nb–O for $ZnWO_4$, $CdWO_4$ and $BiNbO_4$, respectively.

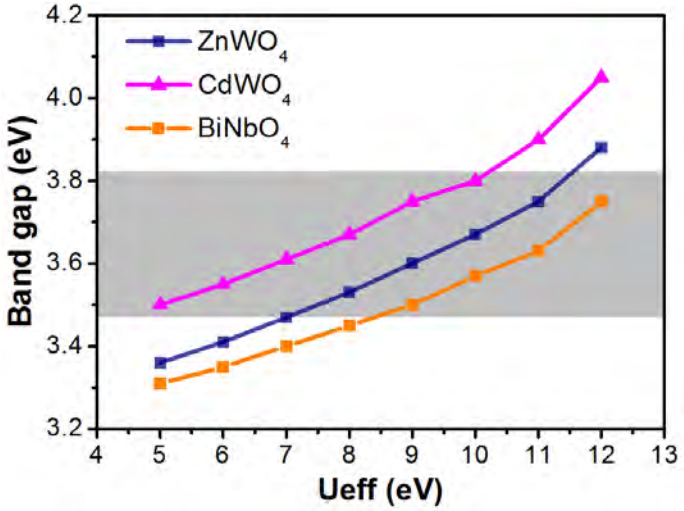

Figure 2. The electronic band gap of bulk $ZnWO_4$, $CdWO_4$ and $BiNbO_4$ against the different U_{eff} values. The shaded area represents the experimental region.

Results and Discussion cont'd

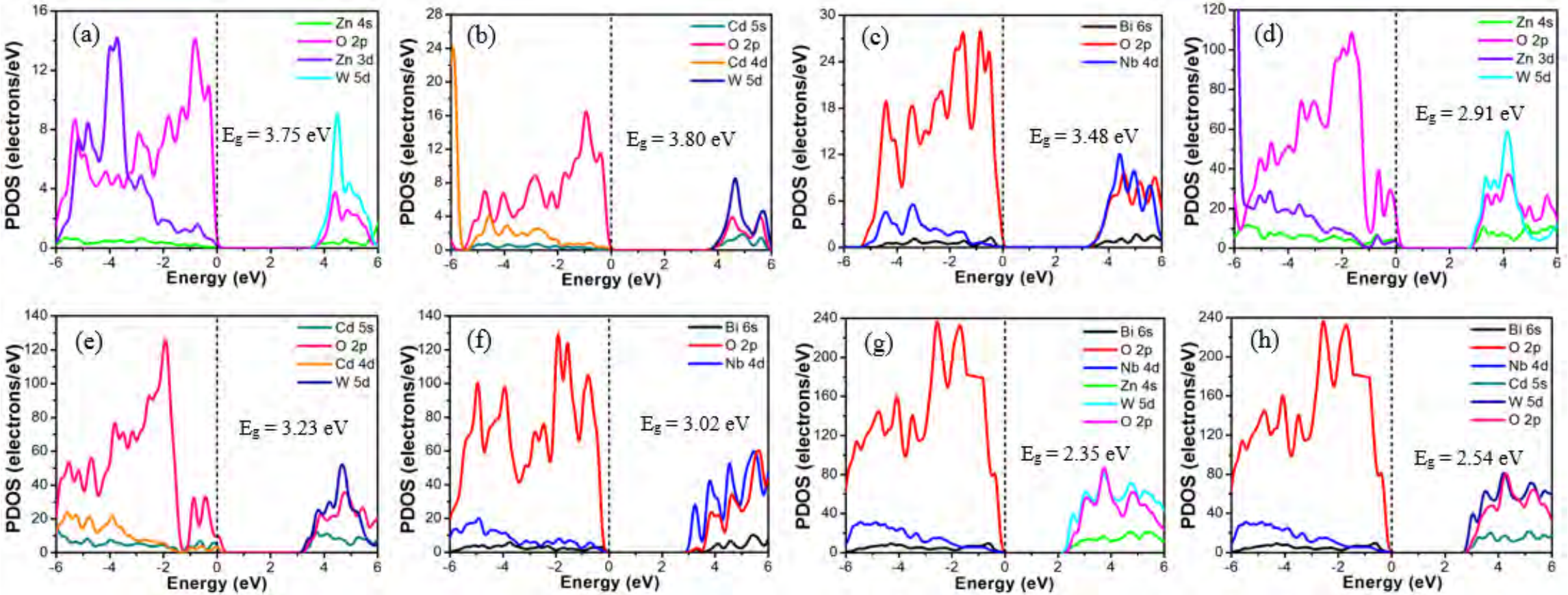

Figure 3. GGA+*U* calculated PDOS of (a) bulk $ZnWO_4$, (b) bulk $CdWO_4$, (c) bulk $BiNbO_4$, (d) $ZnWO_4$(010) surface, (e) $CdWO_4$(010) surface, (f) $BiNbO_4$(010) surface, (g) $BiNbO_4$/ $ZnWO_4$(010) heterostructure and (h) $BiNbO_4$/$CdWO_4$(010) heterostructure. The Fermi level is set to zero eV as a black dashed line.

Results and Discussion contd.

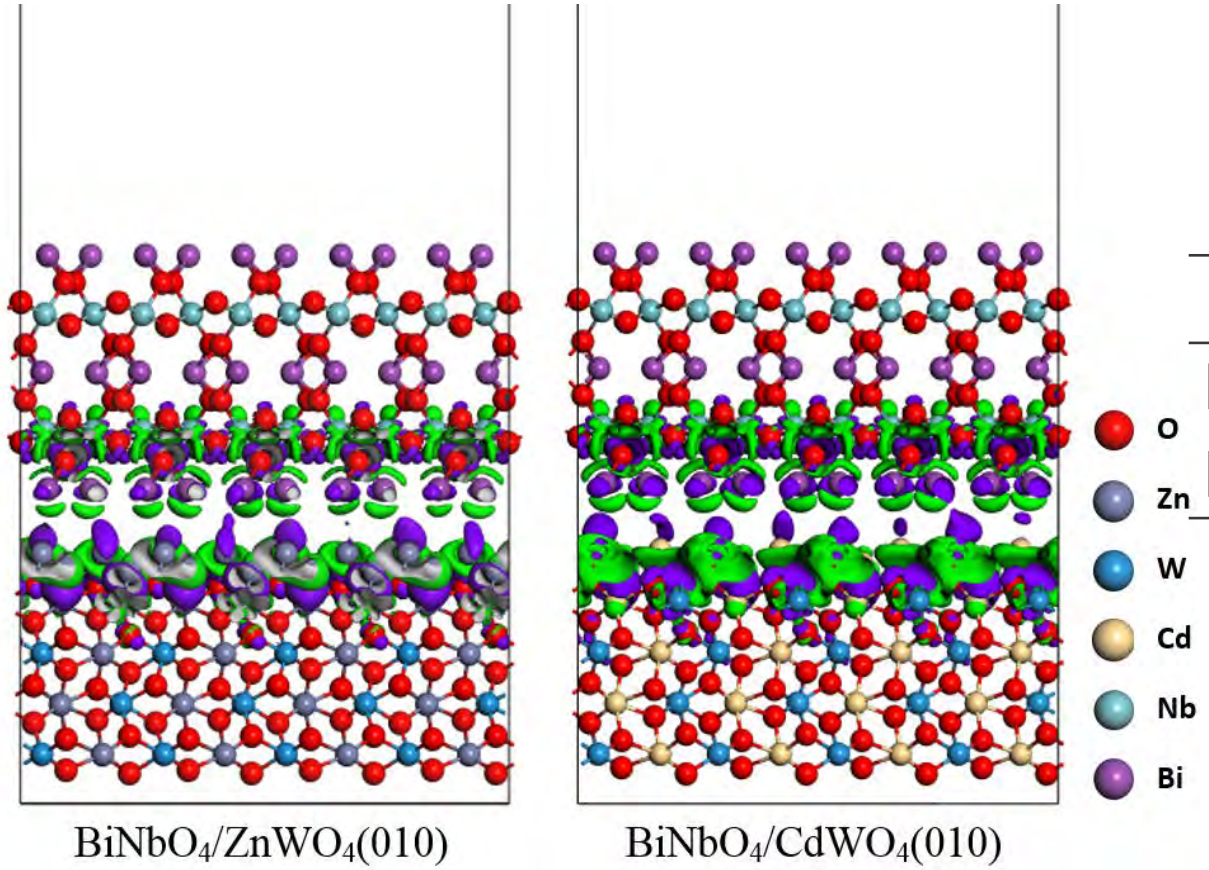

Table 3. The charge transfer (ΔQ), interface distance (d) and adhesion energy (E_{ad}) of the heterostructures systems.

	ΔQ (e)	d(Å)	E_{ad} (eV)
$BiNbO_4/ZnWO_4(010)$	0.28	3.49	–0.26
$BiNbO_4/CdWO_4(010)$	0.05	3.72	–0.58

Figure 4. The three-dimensional charge density difference for the $BiNbO_4/MWO_4(010)$ heterostructures. The green and purple regions signify charge depletion and accumulation, respectively with isosurface value of 0.006 e/Å^3.

Results and Discussion cont'd

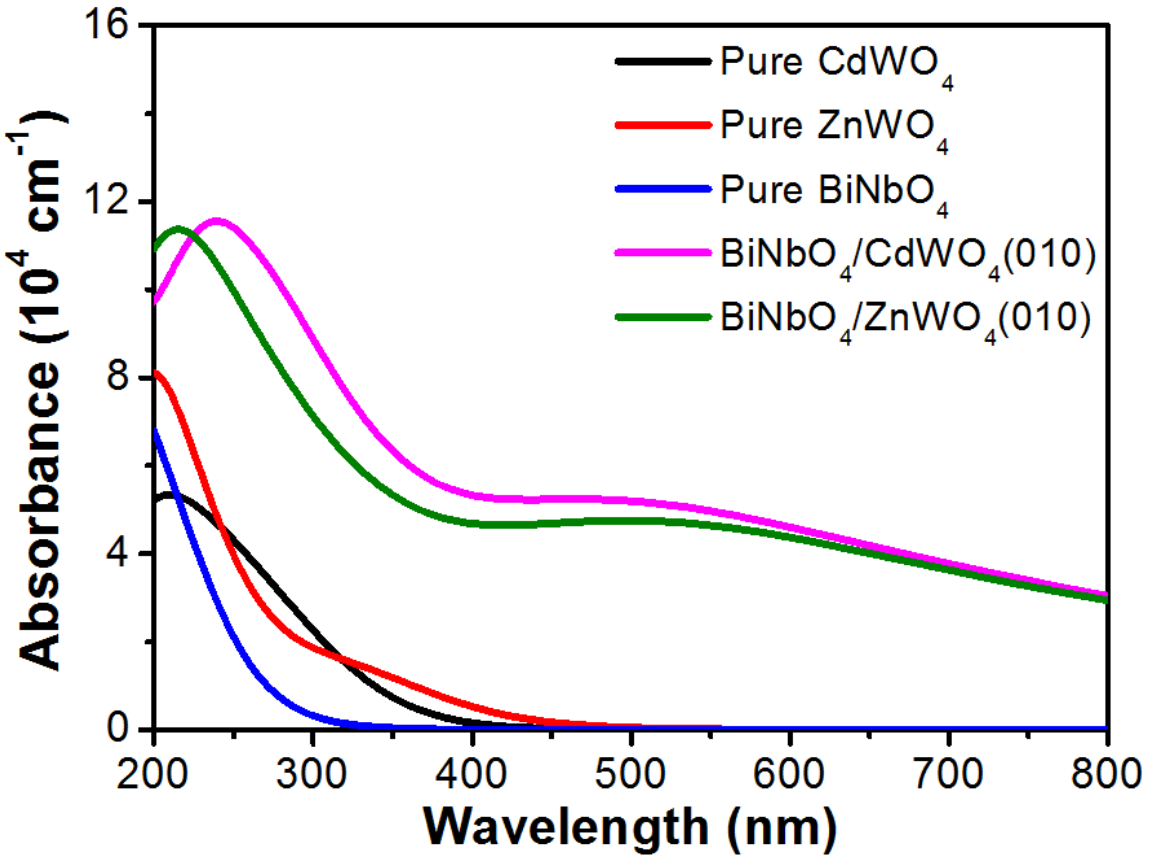

Figure 5. The absorption spectrum of bulk MWO_4, bulk $BiNbO_4$, $BiNbO_4/MWO_4$(010) heterostructures.

Results and Discussion contd.

Table 4. Calculated effective masses of m_e^*/m_o and m_h^*/m_o of bulk $ZnWO_4$, bulk $CdWO_4$, bulk $BiNbO_4$, $BiNbO_4/ZnWO_4$(010) heterostructure and $BiNbO_4/CdWO_4$(010) heterostructure.

Species	m_e^*/m_o	m_h^*/m_o	$D = \frac{m_h^*}{m_e^*}$
$ZnWO_4$	2.13 (Z → Y)	3.43 (Z → Y)	1.61
$CdWO_4$	2.16 (Z → Y)	3.54 (Z → Y)	1.64
$BiNbO_4$	2.08 (G → X)	2.98 (G → X)	1.43
$BiNbO_4/ZnWO_4$(010)	1.07 (G → F)	2.26 (G → F)	2.12
$BiNbO_4/CdWO_4$(010)	1.68 (G → F)	2.58 (G → F)	2.04

Results and Discussion contd.

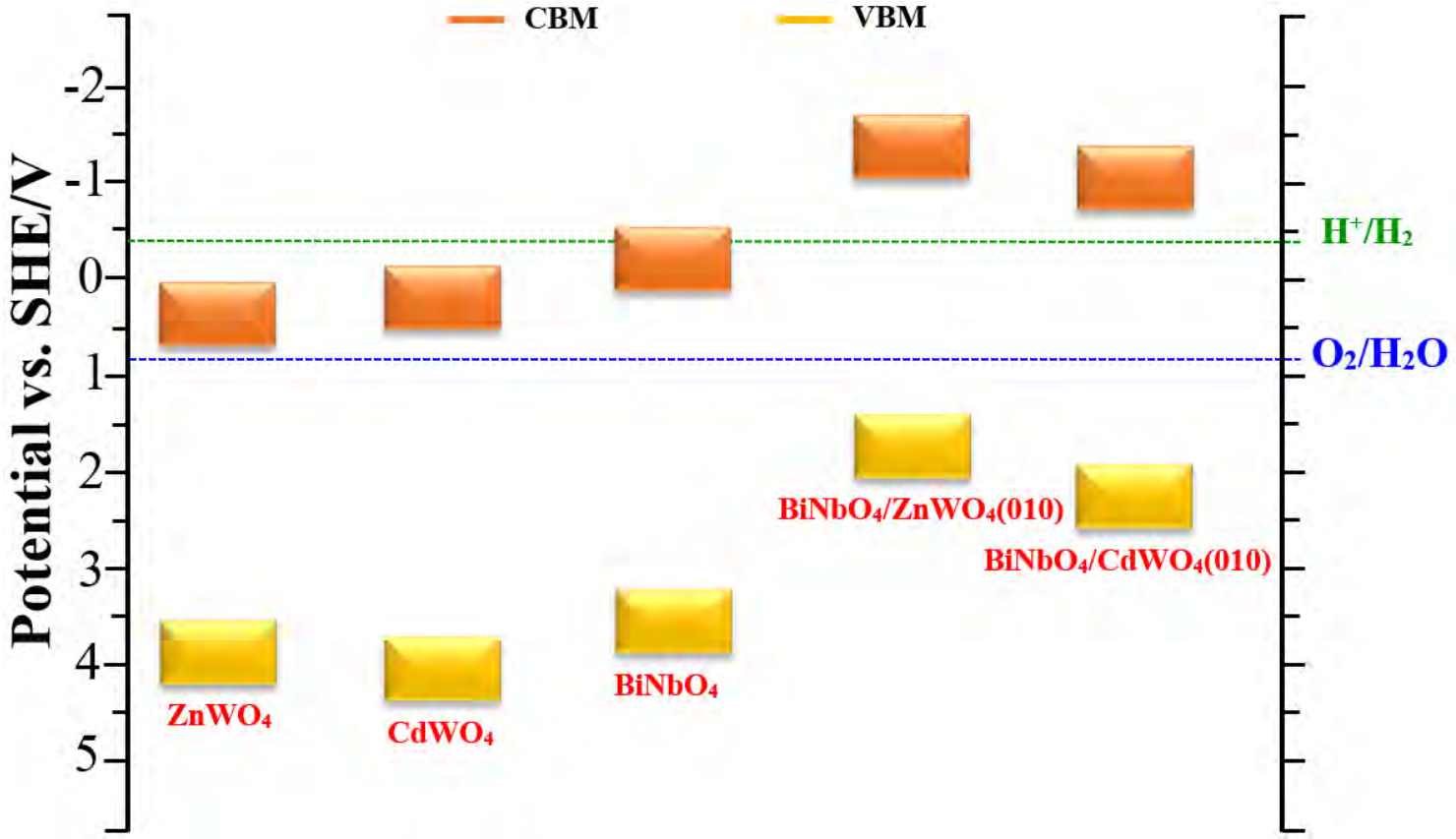

Figure 6. Band edge positions of $ZnWO_4$, $CdWO_4$, $BiNbO_4$, $BiNbO_4/ZnWO_4(010)$ and $BiNbO_4/ CdWO_4(010)$. The two dashed black lines (+0.82 and –0.41 V *versus* SHE) are the oxidation potential of O_2 and the reduction potential of H_2

Conclusions

- The heterostructures show a reduced band gap, low ionisation energy and electron affinity, strong absorption in the visible light region and high charge carriers mobility compared to the pure systems.
- The calculated band edge positions show a type–II staggered band alignment.
- The $BiNbO_4/ZnWO_4(010)$ heterostructure was observed to be a suitable material for the H_2 evolution due to its high reducing power.
- These theoretical studies shed insight on the less–known $BiNbO_4/MWO_4(010)$ heterostructures and the fully explored electronic and optical properties will pave way for future applications in photocatalytic water splitting.

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Thank You all for Your attention