Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

Enhanced photosensitized activity of $BiOCl/Bi_2WO_6$ heterojunction by effective interfacial charge transfer †

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Surface grand potentials calculation

Surface grand potentials can be calculated by:

$$\Omega_S^i = \frac{1}{2S}\left[E_{slab}^i - N_{Bi}\mu_{Bi} - N_w\mu_w - N_o\mu_o\right]$$

with N_{Bi}, N_w, and N_O the number of Bi, W, and O atoms in the slab, μ_{Bi}, μ_w, μ_o the chemical potential of Bi, W, and O atoms and the factor of 1/2 corresponds to the two surfaces of a slab.

Since the surface is in equilibrium with the bulk Bi_2WO_6, we have $\mu_{Bi_2WO_6} = E_{bulk}$, and $\mu_{Bi_2WO_6} = 2\mu_{Bi} + \mu_w + 6\mu_o$. The surface grand potentials can also be expressed as:

$$\Omega_S^i = \frac{1}{2S}\left[E_{slab}^i - N_W E_{bulk} - (N_{Bi} - 2N_W)\mu_{Bi} + (6N_W - N_O)\mu_o\right]$$

If we introduce the variation of the chemical potentials with respect to the reference phases

($\Delta\mu_o = \mu_o - \frac{E_{o_2}^{mol}}{2}$ $\Delta\mu_w = \mu_w - E_w^{bulk}$, respectively)

$$\Omega_S^i = \Phi_i + \frac{1}{2S}\left[-\Delta\mu_{Bi}(N_{Bi} - 2N_w) + \Delta\mu_o(6N_w - N_o)\right]$$

where

$$\Phi_i = \frac{1}{2S}\left[E_{slab}^i - N_W E_{bulk} - (N_{Bi} - 2N_W)E_{Bi}^{bulk} + (6N_W - N_O)\frac{E_{O_2}^{mol}}{2}\right]$$

According to the calculation formula of surface grand potentials, the calculated values Φ_i, Ω_s^i of six possibilities in Fig.S1 (a) are listed in Table SI. O_I terminated surface is the most stable Bi_2WO_6 (010) surface.

Table SI Surface grand potentials of various exposed planes

Exposed plane	Φ_i	Ω_S^i
O_{III}	26.92	26.92
Bi_{II}	26.75	$26.75+(4*\Delta\mu_O)/(2*29.59)$
O_{II}	27.02	$27.02+(4*\Delta\mu_{Bi}+4*\Delta\mu_O)/(2*29.59)$
WO	27.07	$27.07+(4*\Delta\mu_{Bi}+8*\Delta\mu_O)/(2*29.59)$
O_I	13.19	$13.19+(-4*\Delta\mu_{Bi}-8*\Delta\mu_O)/(2*29.59)$
Bi_I	13.28	$13.28+(-4*\Delta\mu_{Bi}-4*\Delta\mu_O)/(2*29.59)$

Boundary limits for the chemical potentials

The oxygen, tungsten and bismuth atoms are not to form condensate on the surface.

Consequently, the chemical potential of each species must be lower than the energy of an atom in the stable phase, so the following non-equation should be apply:

$$\Delta\mu_o = \mu_o - \frac{E_{O_2}^{mol}}{2} < 0$$

$$\Delta\mu_{Bi} = \mu_{Bi} - \frac{E_{Bi}^{bulk}}{2} < 0$$

$$\Delta\mu_w = \mu_w - \frac{E_w^{bulk}}{2} < 0$$

Then formation energy could be calculated as follows:

$$E_{Bi_2WO_6}^f = E_{Bi_2WO_6}^{bulk} - 2E_{Bi}^{bulk} - E_W^{bulk} - 3E_{O_2}^{mol}$$

$E_{Bi_2WO_6}^f$ is the formation energy of Bi_2WO_6 with respect to the Bi atom in the mono bulk structure, W atom in bcc bulk structure and the O atom in the gas phase. The total energy of each term is listed in Table SII. The formation energy of Bi_2WO_6 is calculated as -16.46 eV.

Table SII The total energy of Bi, W, O_2 and Bi_2WO_6 (eV)

Terms	Bi mono bulk	W bcc bulk	O_2 gas	Bi_2WO_6 bulk
Energy (eV)	-3.54	-12.72	-9.86	-65.84

Then the lower bound can be determined by: [1] $2\Delta\mu_{Bi} + 6\Delta\mu_o > -E_{Bi2WO6}^f$. Thus the Bi

chemical potential is within the range from -8.23 eV to 0 eV. Oxygen chemical potential is within the range from -2.74 eV to 0 eV.

Though analyzing the table SI and considering the boundary limits for the chemical potentials, O_I shows the lowest surface energy. Fig.S1 (b) shows the $BiOCl/Bi_2WO_6$ interface with Bi_I-O-Bi_{II} bonds.

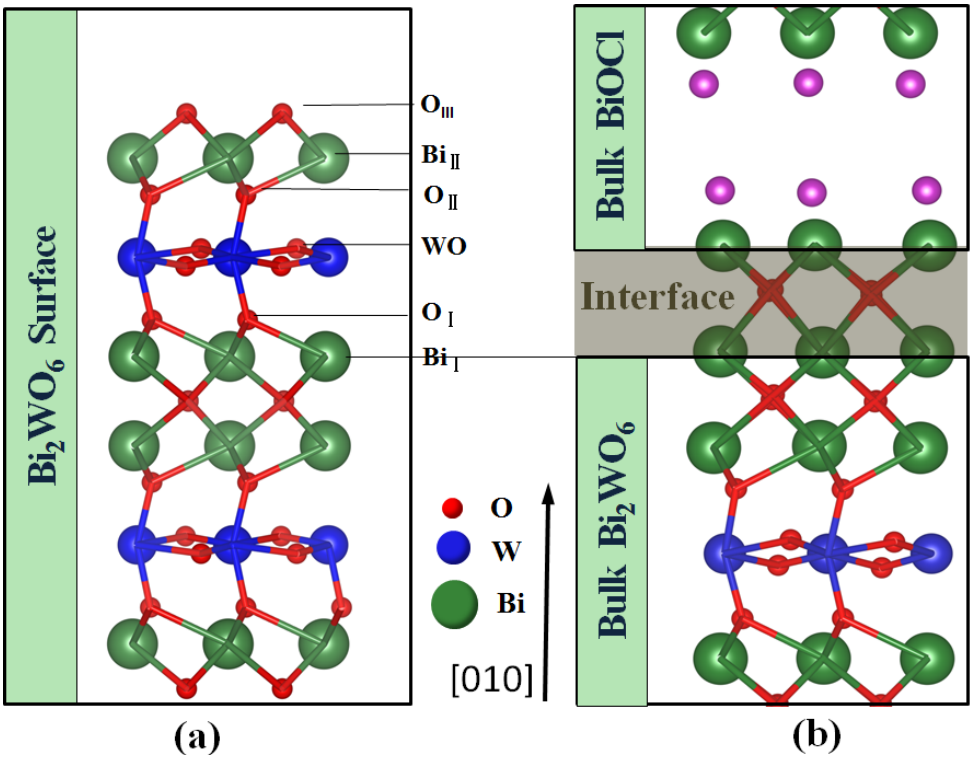

Fig. S1 (a) side-view of Bi_2WO_6 (010) slab with exposed atoms O_I, Bi_I, WO, O_{II}, Bi_{II}, O_{III} (b) optimized structure with Bi_I-O-Bi_{II} bonds as interface.

1 F. Bottin, F. Finocchi and C. Noguera, *Phys. Rev. B,* 2003, **68**, 035418.