Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

An investigation on the role of W doping in $BiVO_4$ photoanodes used for solar water splitting

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Theoretical calculation methods

Adsorption and surface energies calculation.

The adsorption energy (E_{ads}) between surface and adsorbed particles was computed by equation 1.

$$E_{ads} = E_{molecule+surface} - E_{molecule} - E_{surface} \quad (1)$$

"where $E_{molecure+surface}$ is the total energy of the system, including the adsorption molecules and the $BiVO_4$ facet; $E_{molecule}$ is the optimized energy of adsorption molecules, which can be derived from the reference species including H_2O and H_2. For example, $E_{OH^-} = E_{H2O} - 0.5E_{H2}$. The energy of H_2O and H_2 are -468.71 eV and -31.55 eV respectively.[1] $E_{surface}$ is the energy of $BiVO_4$ facet." In the definitions, the higher negative value of E_{ads} indicates a more stable adsorption on the plane. All the calculated energies reported herein include Zero-Point Energy (ZPE) correction.[2] The surface energy (γ) can be calculated by the following equation 2:

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

where E_{slab} is the total energy of the slab model, E_{bulk} is the total energy per unit cell of the bulk, n is the number of unit cells that the slab model contains, and A is the surface area of the slab model.

Table S1. Composition measurement by EDX.

Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
O K	6.48	0.6502	17.42	0.56	64.14
V K	7.90	0.9643	14.31	0.27	16.55
W M	0.81	0.7874	1.80	0.28	0.58
Bi M	34.50	0.9075	66.46	0.57	18.73
Total			100.00		100.00

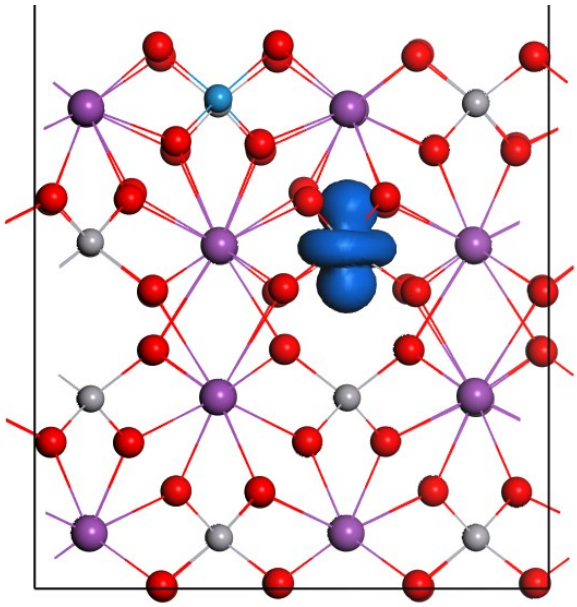

Fig. S1. The Spin density map of WBVO.

Spin density map of W-doped $BiVO_4$ shows the localization of an electron on V. The spin density isosurface (0.05 e $bohr^{-3}$) of an isolated band is shown in blue.

Table S2. Formation energy of W substitution.

	E_{WBVO}	E_{PBVO}	E_W	E_V	E_F
W replacing V	-62023.77	-62067.41	-1935.87	-1977.67	1.85
interstitial W1	-63998.10	-62067.41	-1935.01	-1977.67	4.32
interstitial W2	-63999.20	-62067.41	-1935.01	-1977.67	3.22

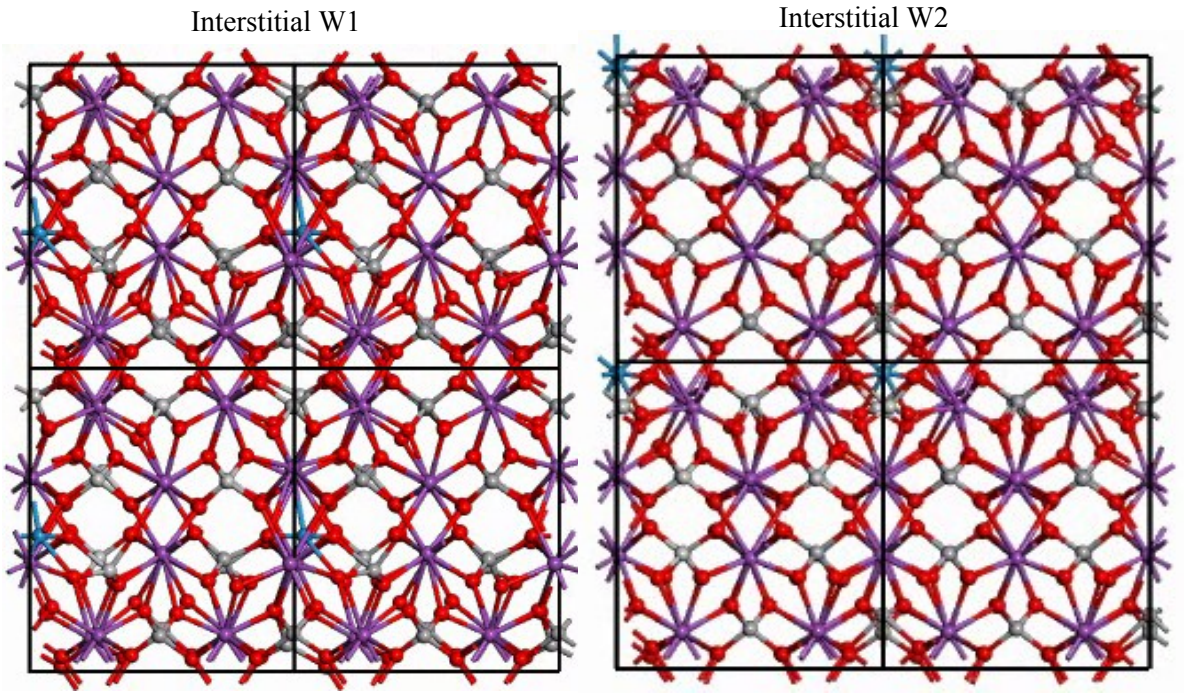

Fig. S2. Two different sites of interstitial substitution of V by W.

The formation energy (E_F) of W replacing V atom can be estimated by equation 3;

$$E_F = E_{WBVO} - E_{PBVO} - E_w + E_v \quad (3)$$

And the formation energy (E_f) of W interstitial substitution can be estimated by equation 4;

$$E_F = E_{WBVO} - (E_{BVO} + E_W) \quad (4)$$

where E_{WBVO} is the total energy of W-doped bulk and surface, E_{PBVO} is the total energy of $BiVO_4$ bulk and surface, E_w is the one-atom energy of W (Space Group: 229) and E_v is the one-atom energy of V (Space Group: 229). Based on the calculation, interstitial W is unlikely to occur due to its high formation energy.

References

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2. Z.-Q. Huang, B. Long and C.-R. Chang, Catal. Sci. Technol., 2015, **5**, 2935-2944.