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Electronic Supporting Information

Why does F-doping enhance the photocatalytic water-splitting performance of *m*$BiVO_4$: a density functional study

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S1. Computational methods

To further evaluate the stabilities after introducing the F atoms, the impurity formation energy (E_{form}) is calculated according to the following formula[33]:

$$E_{form} = E_{doped} - E_{pure} - \mu_F + \mu_O \quad (1)$$

Where, E_{pure} and E_{doped} are the total energies of pure and F-doped *m*$BiVO_4$ systems, respectively. μ_F and μ_O are the chemical potentials of F and O atoms, respectively. Here, gaseous fluorine (F_2) and gaseous oxygen (O_2) are used to determine the chemical potentials : μ_F=1/2μ(F_2), μ_O=1/2μ(O_2).

Table S1 The formation energies (E_{form}) of the F-doped *m*$BiVO_4$ (010) and (110) surfaces

	(010) surface			**(110) surface**			
	F@O1	F@O2	F@O3	F@O1	F@O2	F@O3	**F@O4**
E_{form} **/eV**	-0.69	-0.35	-0.23	-0.64	-0.61	-0.55	-0.19

To avoid the formation of hydrogen bonds between H_2O molecules and calculate the adsorption energy accurately, the (2×2) supercell for (010) and (110) surfaces were used to adsorb one H_2O molecule. All the possible adsorbed models (including water molecule parallel lying, v-shape and inverted v-shape respectively adsorbed on top sites of the V, Bi and O atoms) were optimized, and the most stable adsorbed models on the pure (010) and (110) surfaces were presented in Fig.10.

the adsorption energy (E_{ads}) is calculated by the following definition:

$$E_{ads} = E(H_2O/slab) - [E(H_2O) + E(slab)] \quad (2)$$

where E(H_2O/slab), E(slab) and E(H_2O) are the total energy of the water adsorbed slab, the total energy of the pure or F-doped slab surfaces without water adsorption and the total energy of a relaxed water molecule, respectively. The calculated values of E_{ads} are listed in Table S2.

Table S2 The adsorption energies (E_{ads} /eV) of water on the pure and F doped (010) and (110) surfaces.

	(010) surface		(110) surface		
	Pure	F@O1	Pure	F@O1	F@O2
E_{ads} /eV	-0.50	-1.45	-0.55	-1.32	-1.49

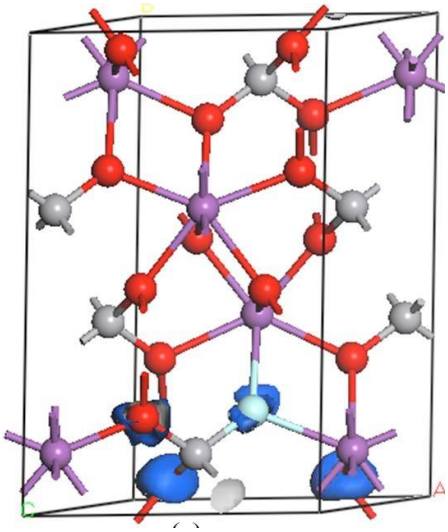

Fig. S1 the spin partial density of states for F-doped *m*$BiVO_4$ bulk.