

## The quantum size and spin-orbit coupling effect in $\text{BiVO}_4$ with several atomic layers studied by density functional theory

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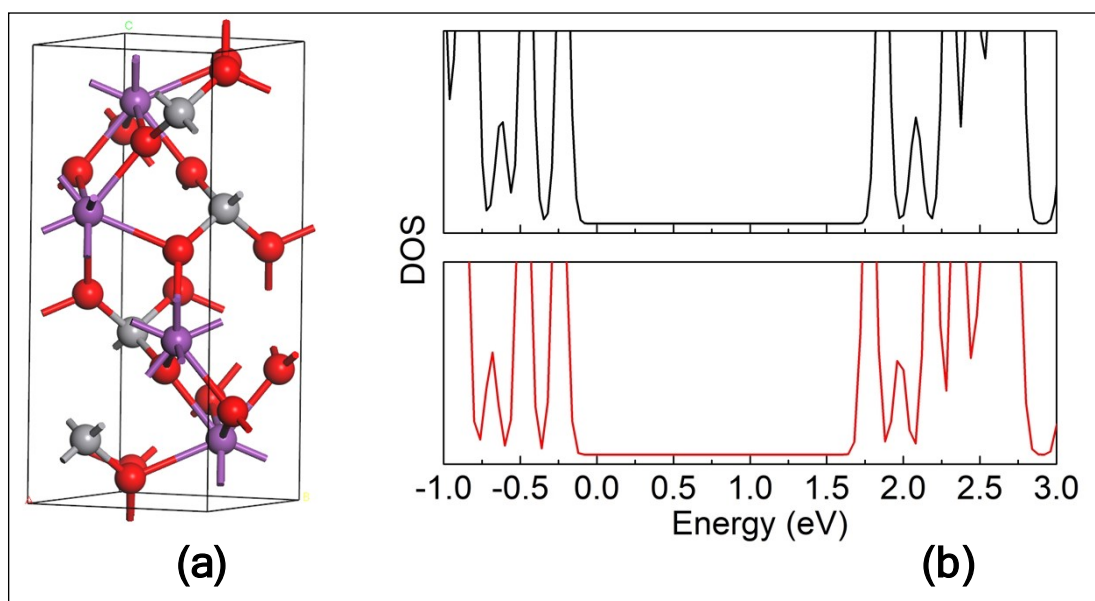


Figure S1. (a) The geometry structure and (b) density of state (DOS) of the bulk BVO. In the DOS, the black line is the result without spin-orbit coupling (SOC), and the red line is the result with SOC. The red, purple, and grey spheres are O, Bi, and V atoms.

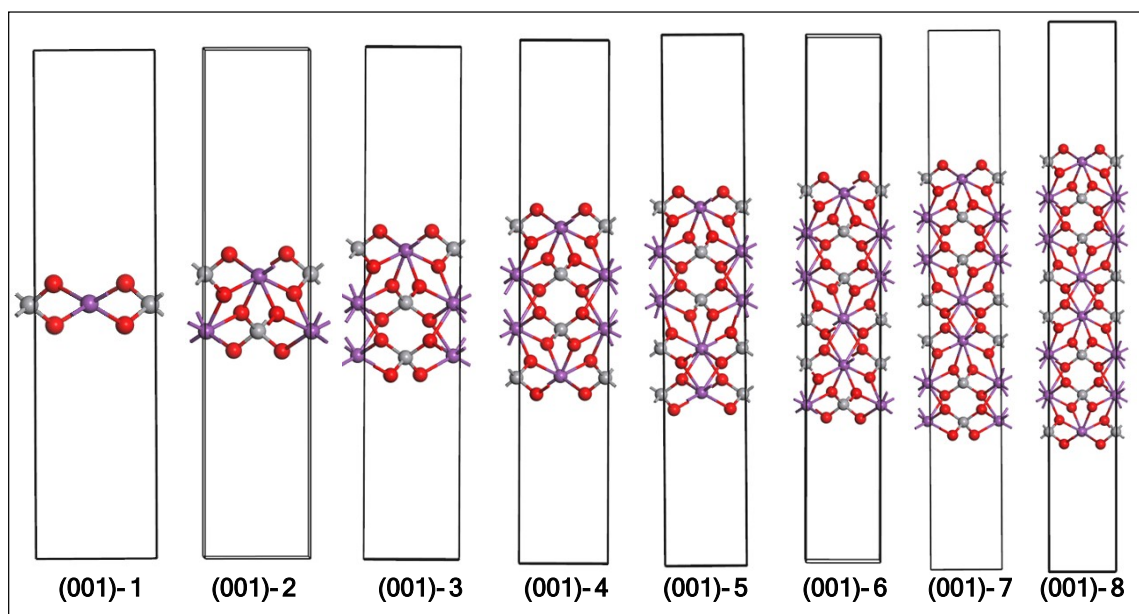


Figure S2. The geometry of (001) slabs. The red, purple, and grey spheres are O, Bi, and V atoms.

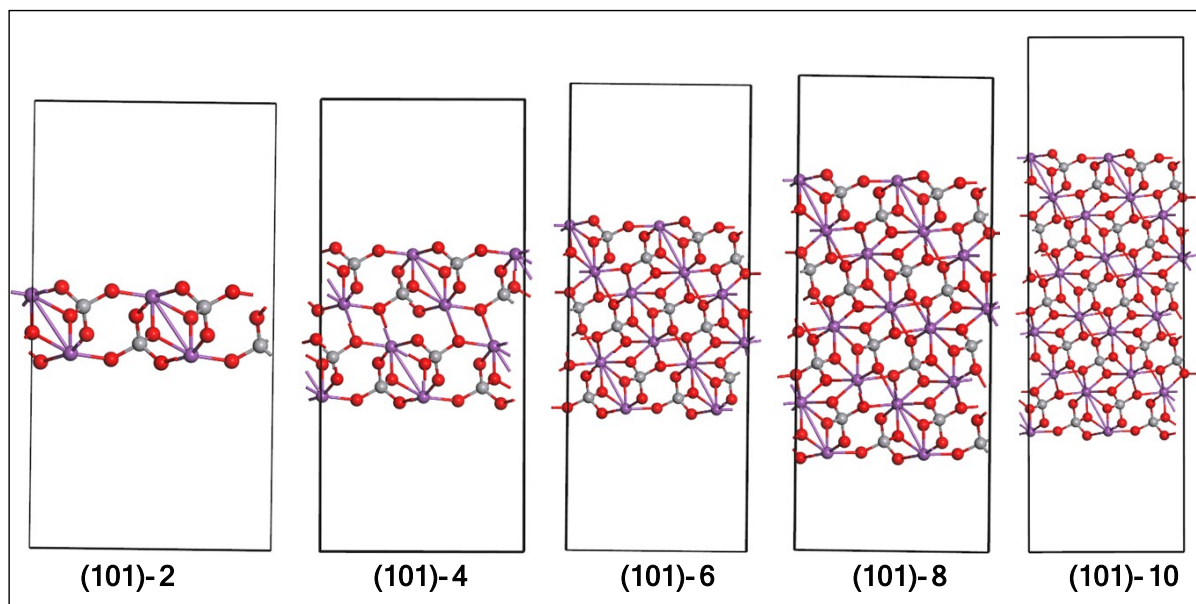


Figure S3. The geometry of (101) slabs. The red, purple, and grey spheres are O, Bi, and V atoms.

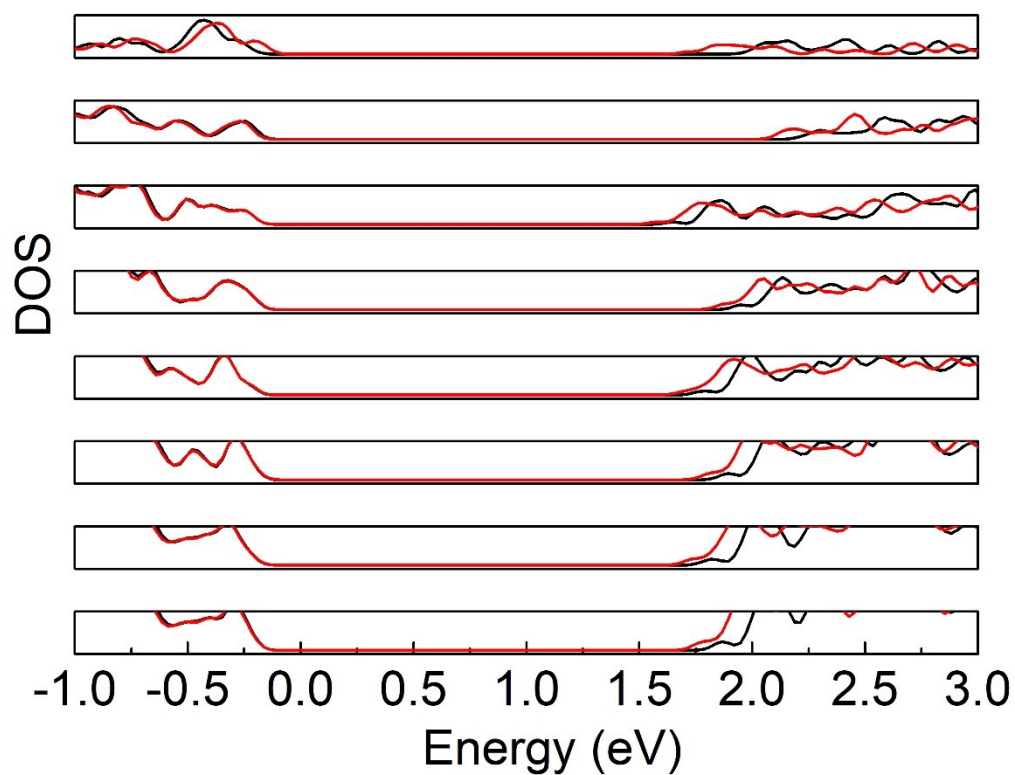


Figure S4. The DOS of all the (001)-slabs. From top to the bottom is the DOS of 1 to 8 Bi layers slab. The black line is the result without spin-orbit coupling (SOC), and the red line is the result with SOC.

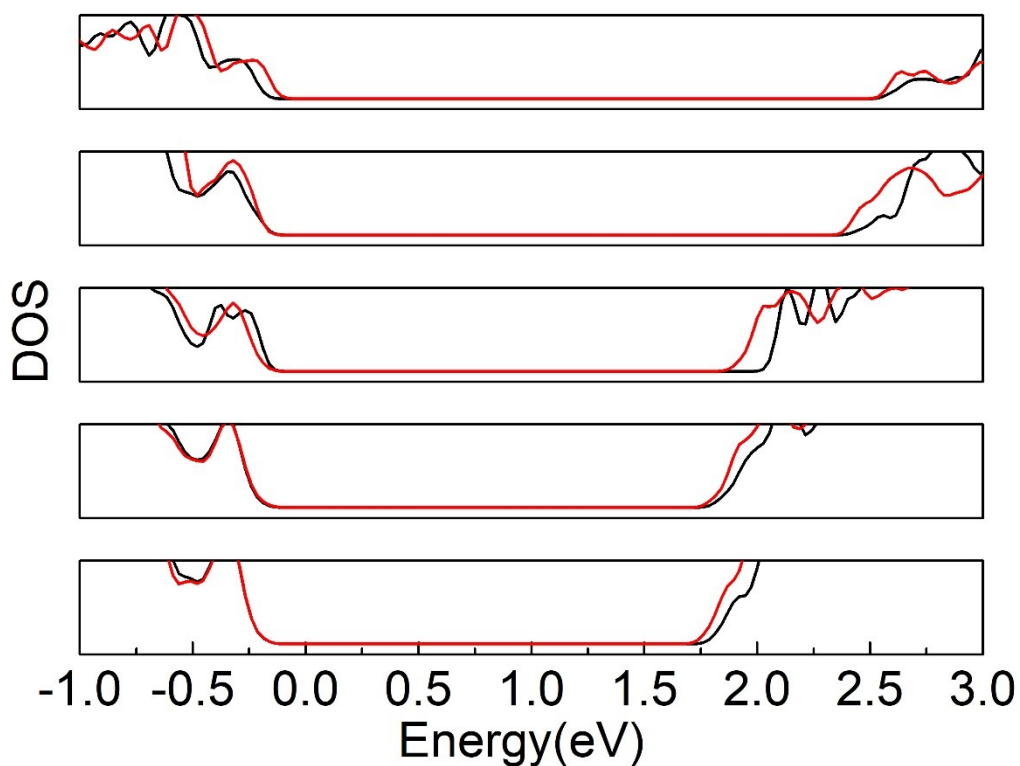


Figure S5. The DOS of all the (101)-slabs. From the top to the bottom is the DOS of 2, 4, 6, 8 and 10 Bi layers slab. The black line is the result without spin-orbit coupling (SOC), and the red line is the result with SOC.

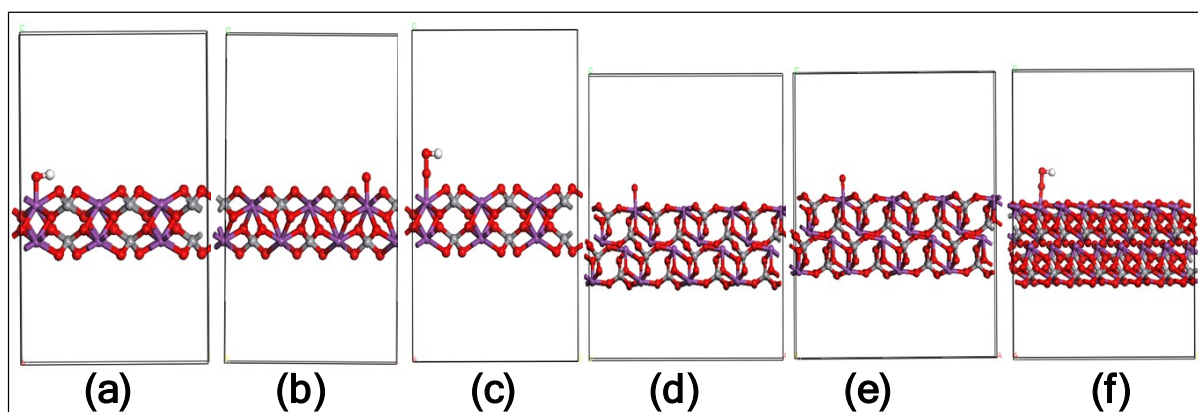


Figure S6. The structure of OER intermediates (a, d)  $\text{OH}^*$ , (b, e)  $\text{O}^*$ , and (c, f)  $\text{OOH}^*$  on (001) and (101) slabs respectively. The red, purple, grey, and white spheres are O, Bi, V, and H atoms.

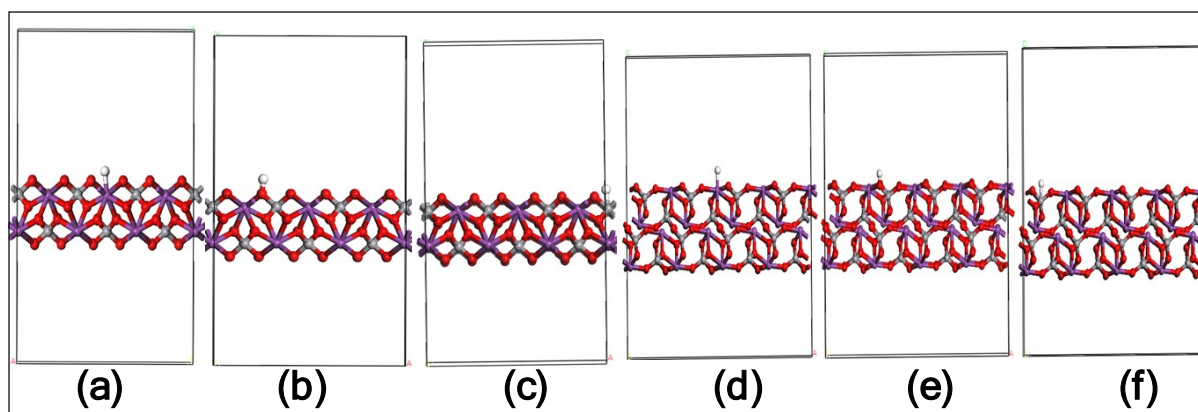


Figure S7. The structure of HER intermediates (a, d) H\* on Bi site, (b, e) H\* on O site, and (c, f) H\* on V site on (001) and (101) slabs respectively. The red, purple, grey, and white spheres are O, Bi, V, and H atoms.