Behavior of electron transport in P-doped of BiVO$_4$: a computational study
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Abstract: Recently, bismuth vanadate (BiVO$_4$) has emerged as a promising photoanode material for photocatalytic water splitting, which can absorb visible light with a suitable bandgap energy of ~2.4 eV. However, BiVO$_4$ usually shows a low photocatalytic activity owing to poor charge-transport characteristics and weak surface adsorption properties. Impurities doping into the crystal lattice of semiconductors is one way to improve the photocatalytic activity, leading to changing in geometric properties, electronic properties and behavior of charge carrier transport. In this work, the behavior of the electron transport in phosphorus-doped BiVO$_4$ will be explored using density functional theory (DFT) calculations. We used the DFT+U method to correct the electron self-interaction error in DFT calculations. Marcus theory of electron transfer was employed to describe the behavior of electron transport in P-doped BiVO$_4$. Computations show that the excess electron is self-trapped at a V$^{5+}$ site as a small polaron in BiVO$_4$ supercell. The activation energies of the polaron migration are in the range of 0.3 eV in all possible migration paths. Substitution of vanadium by phosphorus leads to a local lattice distortion in the structure which could in turn reduce the polaron migration barriers and enhance charge separation in the doped BiVO$_4$.

Keywords: P-doped BiVO$_4$; Density functional theory; Photocatalyst