First principles investigation of the structural-phase and impurity-doping effects on the photocatalytic performance of bismuth vanadate

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Renewable sources of energy are increasingly needed and solar production of hydrogen fuel from water offers significant potential to contribute to these needs. Bismuth vanadate ($BiVO_4$) has received much interest as a promising visible-light-active photocatalyst for water splitting and pollutant decomposition. $BiVO_4$ has been found to exhibit phase-dependent photocatalytic activity. For instance, the monoclinic phase (*m*-$BiVO_4$) exhibits much higher activity than the tetragonal phase (*t*-$BiVO_4$), although their main difference is a slight structural distortion in *m*-$BiVO_4$. Besides the underlying reason for the superior performance of *m*-$BiVO_4$ over *ts*-$BiVO_4$, mechanisms underlying the enhanced photocatalytic activity of *m*-$BiVO_4$ through incorporation of impurities such as phosphorous still remain poorly understood. For instance, doping of W, Mo or P into $BiVO_4$ has been experimentally found to lead to a significant increase in the photooxidation current of water.

In this talk, we will present theoretical evidence for phase dependence in the localization and transport of excess charge carriers, based on hybrid density functional theory calculations; this may shed some insight into why *m*-$BiVO_4$ and *t*-$BiVO_4$ exhibit a considerable difference in photocatalytic performance. In addition, the effect of impurity doping will be discussed with our theoretical explanation and prediction. The improved understanding may offer important guidance for the rational design of $BiVO_4$-based materials for high efficiency solar-powered hydrogen generation.