論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Functionalizing Bismuth Vanadate Photocatalyst by Surface Modification and Band Position Tuning
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出典(和文)	学位:博士(学術), 学位授与機関:東京工業大学, 報告番号:甲第12592号, 授与年月日:2023年9月22日, 学位の種別:課程博士, 審査員:宮内 雅浩,中島 章,保科 拓也,磯部 敏宏,山口 晃
Citation(English)	Degree:Doctor (Academic), Conferring organization: Tokyo Institute of Technology, Report number:甲第12592号, Conferred date:2023/9/22, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）

Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	材料 材料	系 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of	（ 学術 ）
学生氏名： Student's Name	Yang Yue		審査員主査： Chief Examiner	宮内雅浩	

要旨（英文 800 語程度）

Thesis Summary（approx.800 English Words ）

The thesis entitled "Functionalizing Bismuth Vanadate Photocatalyst by Surface Modification and Band Position Tuning" consists of six chapters.

In the first chapter, "Introduction", I provide a brief overview of photocatalysts. Photocatalysts have been widely used for solar fuel generation and environmental purification. There are two requirements to initiate photocatalytic reactions: first, the incident photon energy must be higher than the bandgap value, second the conduction band and valence band positions of semiconductors must be higher than the redox potential of the desired reactions. Solar light is primarily composed of visible light (43% in solar light), which has a lower photon energy compared to UV-light (5% in solar light). These facts result in a trade-off between narrow band gaps and high redox potentials in the development of photocatalysts. Previous research has primarily focused on sensitizing wide gap semiconductors to become visible light responsive through doping or dye sensitization. In contrast, this research aims to functionalize narrow gap photocatalysts. Narrow gap photocatalysts are visible light sensitive but limited in photocatalytic reactions due to insufficient redox potentials of photogenerated carriers. Therefore, the objective of this research is to functionalize narrow gap photocatalysts. I choose bismuth vanadate ($BiVO_4$) as the target photocatalyst as it was widely studied as a green light active photocatalyst but limited for water oxidation reaction. The following three chapters discussed three strategies for functionalizing the $BiVO_4$ photocatalyst: surface modification for gaseous organic decomposition (Chapter II), valence band position tuning for higher oxidation power of photogenerated holes(Chapter III), and band structure tuning through quench treatment (Chapter IV).

In the second chapter, "Surface Modification of $BiVO_4$ Photocatalyst for Organic Decomposition", I describe the modification of Fe(III) nanoclusters on the surface of $BiVO_4$ to functionalize it for gaseous organic decomposition reactions. The pristine $BiVO_4$ photocatalyst cannot initiate the electron reduction reaction of oxygen due to the insufficient reduction energy of photogenerated electrons. By surface modifying Fe(III) nanoclusters, the photoexcited electrons accumulate at the Fe(III) nanoclusters, subsequently activating the multi-electron reduction reaction of oxygen, which requires much lower energy compared to the one-electron reduction reaction. The surface modification of Fe(III) nanoclusters successfully activates $BiVO_4$ for gaseous organic decomposition reactions, making it the first reported green light active photocatalyst for environmental purification.

In the third chapter, "Bandgap Widening through Doping for Improving the Photocatalytic Oxidation Ability of $BiVO_4$ Photocatalyst," I focus on tuning the valence band position of $BiVO_4$ to achieve higher oxidation power. I propose an orbital dilution strategy for valence band position tuning and validate it by first principles calculations and experimental studies. The valence band of $BiVO_4$ is composed of hybrid Bi-s and O-p orbitals, resulting in an upward shifted valence band position. To enhance the oxidation power of photogenerated holes, I dilute the Bi component by

doping lanthanum (La) ions. Through my first principles calculations and experimental characterizations, I confirm a downward shift of the valence band top over the La-doped $BiVO_4$ sample. The photocatalytic oxidation performance is then where the La-doped sample exhibits superior oxidation performance compared to pure $BiVO_4$. This work offers insight into doping-induced bandgap widening for improving photocatalytic performances.

In the fourth chapter, "Quench Treatment for Band Structure Tuning", I develop a general strategy for band structure engineering. While the surface modification strategy discussed in Chapter II focuses on altering the reduction reaction to the desired one, and the orbital dilution strategy discussed in Chapter III is related to the specific valence band composition of $BiVO_4$, Chapter IV discusses quench treatment as a more general strategy for band tuning. Previous research indicates a relationship between lattice constant and band structure changes, inspiring me to explore band engineering by tuning the unit cell. Through my first principles calculations, I observe a narrowed bandgap and an upward shifted valence band position in a contracted $BiVO_4$ unit cell. I then synthesize the $BiVO_4$ materials and conduct quench treatment for further investigation. The quenched material exhibits a smaller unit cell volume compared to the original sample, and further characterization confirms a narrower bandgap and an upward shifted valence band position, consistent with the first principles calculations. Although the quench-induced unit cell volume change is recoverable, this work provides valuable insights into tuning lattice constants for band engineering. In terms of practical application, further research is necessary to determine appropriate substrates that can maintain the quench-induced changes.

In the fifth chapter, "Philosophical Contributions", I discuss the philosophical contributions of this work. Instead of focusing on well-studied sensitizing wide gap semiconductors to become visible light sensitive, this work concentrates on functionalizing narrow gap semiconductors using $BiVO_4$ as an example. In terms of scientific contributions, the proposed orbital dilution strategy allows fine-tuning of the valence band of $BiVO_4$, and this strategy can be generalized to other photocatalysts whose valence bands are composed of hybrid orbitals. Regarding quench treatment for band engineering, I demonstrate that it can effectively tune the crystal lattice, thereby influencing the band structure. These band structure changes also influence the photocatalytic reactions. This strategy is applicable to other photocatalysts, and further studies on choosing suitable substrates to maintain the strain change would facilitate practical applications. In terms of industrial contributions, modifying Fe(III) nanoclusters activate $BiVO_4$ for organic decomposition, making it the first reported green light active photocatalyst for environmental purification. Considering the significant portion of green light in solar spectra and indoor illumination, this work greatly expands the utilization of photocatalysts for environmental purification.

In the sixth and final chapter, I provide a summary of this thesis, which focuses on functionalizing narrow gap semiconductors using $BiVO_4$ as an example.

In summary, I successfully functionalized $BiVO_4$ for organic decomposition reactions through surface modification with Fe(III) nanoclusters and achieved band edge position tuning by employing the orbital dilution strategy and quench treatment.