



# HOKKAIDO UNIVERSITY

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# 学位論文内容の要旨

博士の専攻分野の名称

博士（理学）

PHILO Davin

## 学位論文題名

### Structural Engineering and Surface Modulation of Monoclinic BiVO<sub>4</sub> for Efficient Visible-Light-Driven Photocatalysis

(単斜晶 BiVO<sub>4</sub> の構造制御および表面修飾による効率的な可視光応答光触媒反応に関する研究)

The production of renewable green energy stocks by harnessing unlimited solar energy via artificial photosynthesis (APS) technology has been recognized as one of the best and most adaptable solutions for addressing the global energy crisis and environmental problems. Among many photocatalyst candidates, monoclinic bismuth vanadate (BiVO<sub>4</sub>) semiconductor has attracted growing interest as one of the most promising and advanced materials for various APS applications. Nonetheless, the traditional monoclinic BiVO<sub>4</sub> photocatalyst still manifests some downsides, such as poor charge carrier dynamics, relatively low surface area, and the absence of innate reactive sites, yielding monoclinic BiVO<sub>4</sub> with unsatisfactory photocatalytic conversion efficiencies. With that being the case, this thesis aims to rationally design some superior monoclinic BiVO<sub>4</sub> photocatalysts via structural engineering and surface modulation for highly efficient visible-light-driven photocatalysis. Accordingly, some facile and smart methods were effectively employed during the fabrication process, paving the way for manipulating and modulating the unique properties of the as-synthesized monoclinic BiVO<sub>4</sub> photocatalyst. Furthermore, some in-depth investigations to probe the origin of the properties variations and enhanced photocatalytic performance are also presented and discussed comprehensively.

In chapter 1, a general background about heterogenous photocatalysis and a brief overview about monoclinic BiVO<sub>4</sub> photocatalyst are introduced. Furthermore, an extensive discussion regarding some prospective photocatalytic applications and the unique properties of monoclinic BiVO<sub>4</sub> photocatalyst along with some strategies to control and modulate those properties are presented.

In chapter 2, a cooperative strategy is represented that enables 2D structure tailoring and lattice distortion engineering simultaneously over a BiVO<sub>4</sub> photocatalyst for efficient visible-light-driven OER. Specifically, the lattice distortion engineering was achieved through the introduction of sodium (Na<sup>+</sup>) additive during the ion exchange process. Structural characterizations suggest the formation of ultrathin 2D monoclinic BiVO<sub>4</sub> nanoflakes (BVO NFs) with

shrank V–O and elongated Bi–O bonds. Mechanistic investigations reveal the advantages of ultrathin 2D features for exposing more active (010) facets and shortening the required migration distance for charge carriers to reach the catalytic surface. More importantly, the lattice distortion effect is found to crucially govern the charge carrier dynamics and surface behavior of BiVO<sub>4</sub> photocatalyst, endowing the optimized sample with an outstanding photocatalytic OER performance triggering up to 69.4% apparent quantum efficiency (AQE) over Fe<sup>3+</sup> sacrificial solution. These findings highlight the functional application of morphology and dimensional modification, as well as lattice distortion engineering in synthesizing superior monoclinic BiVO<sub>4</sub> photocatalyst for efficient visible-light-driven water oxidation.

In chapter 3, following the previous chapter, an in-depth investigation to probe the effect of lattice distortion peculiarly to the catalytic OER over the (010) surface of monoclinic BiVO<sub>4</sub> crystals is represented. By initially engaging the ATR-IR spectroscopy to analyze the interaction between the as-prepared monoclinic BiVO<sub>4</sub> sample and water suspension under light irradiation, some reaction intermediates structures were identified, by which a surface OER mechanism could be reasonably deduced. Correspondingly, the first principal calculations for Gibbs free energy of the intermediate structures on the (010) facet of monoclinic BiVO<sub>4</sub> slabs unravel the decrease in the reaction energy barrier as the degree of lattice distortion increases, thus affirming the benefit of lattice distortion effect over the catalytic surface reaction of the water oxidation process. Furthermore, by employing the first-principal molecular dynamic simulations, the oxidizability of some key OER intermediates and the spontaneous water dissociative adsorption process over the (010) surface of the monoclinic BiVO<sub>4</sub> slab model are inspected and discussed in detail.

In chapter 4, an effective oxygen vacancy-mediated size engineering strategy over the well-dispersed palladium (Pd) metal photodeposited on the surface of monoclinic BiVO<sub>4</sub> photocatalyst for efficient visible-light-driven ORR is demonstrated. By simply adjusting the pH during the fabrication process, various monoclinic BiVO<sub>4</sub> photocatalyst with different degrees of oxygen vacancy were successfully synthesized, as confirmed by the spectroscopy characterizations. Upon the selective photodeposition of Pd metal over the (010) surface of the monoclinic BiVO<sub>4</sub> samples, it was discovered that the higher the amount of oxygen vacancy the smaller the size of Pd, which would be beneficial for increasing the number of active sites and thus triggering more swift catalytic surface reaction. Therein, the optimized Pd-BiVO<sub>4</sub> sample was able to realize an excellent photocatalytic H<sub>2</sub>O<sub>2</sub> production up to 2.35 mM/h, accomplishing the state-of-the-art AQE of 19.2% at 420 nm in photocatalytic H<sub>2</sub>O<sub>2</sub> production over BiVO<sub>4</sub>-based materials. This study sets a milestone and also provides some insights into the delicate design of Pd metal-monoclinic BiVO<sub>4</sub> composites for more efficient H<sub>2</sub>O<sub>2</sub> photosynthesis.

In chapter 5, an overall summary of this dissertation work is presented. This thesis carries out some systematic study on structural engineering and surface modulation of monoclinic BiVO<sub>4</sub> for efficient visible-light-driven photocatalysis. More importantly, this thesis emphasizes the great importance and significance of controlling and exploiting the unique properties of monoclinic BiVO<sub>4</sub>. It is unraveled that, by doing so, it would greatly enhance the charge carrier dynamics and/or provide some necessary reactive sites, thus effectively satisfying the fundamental requirements for promoting more efficient artificial photosynthesis. The findings in this study sheds new light on the design and fabrication of high-performance monoclinic BiVO<sub>4</sub>-based materials for various photocatalytic applications.