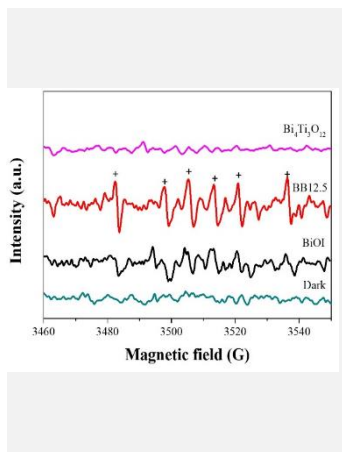


Highly selective photocatalytic oxidation of veratryl alcohol by bandstructure modulation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ through heterojunctions

ORAL
Ph.D. Student: N
Journal: NONE

J.C. Murillo-Sierra¹, D. Contreras², D. Briceño². (1) Facultad de Ciencias Naturales, Matemáticas y Medio Ambiente, Universidad Tecnológica Metropolitana, Las Palmeras 3360, Santiago de Chile, Chile, jcmurillos@utem.cl. (2) Facultad de Ciencias Químicas, Universidad de Concepción, Edmundo Larenas 129, Concepción, Chile



In this work, a straightforward method for synthesizing heterojunction photocatalysts using $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and BiOI, combining hydrothermal and co-precipitation techniques is presented. The synthesized composites were used in the selective oxidation of veratryl alcohol, to produce veratraldehyde—a high-value chemical. Experimental findings demonstrated that the BiOI/ $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ heterojunction (12.5% BiOI) exhibited remarkable activity, with a veratraldehyde yield 5.4 and 27.2 times higher than those of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and BiOI alone, respectively. Mechanistic investigations indicated that this enhanced performance was attributed to improved separation of charge carriers and suppression of reactive oxygen species formation, achieved through modulation of the band structure. This research suggests a sustainable approach to lignin valorization, offering a pathway to produce valuable chemicals in an environmentally friendly manner.

Introduction

Heterogeneous photocatalysis has become a focal point for both the scientific and industrial communities in recent years due to its numerous advantages, including its reliance on renewable energy sources and its ability to operate under environmentally friendly conditions such as atmospheric pressure and ambient temperature. This technology has been utilized for converting lignocellulosic biomass into high-value compounds and green hydrogen [1]. However, its main challenges include high rates of electron-hole pair recombination and low selectivity due to the formation of highly oxidizing reactive oxygen species[2].

In this context, the development of heterostructured materials offers a promising approach to addressing these challenges by efficiently separating charges and modulating band structures. This results in improved efficiency in charge carrier generation and modification of the photocatalytic system's reactivity [3]. Consequently, biomass conversion into valuable products is greatly enhanced, achieving higher conversion rates and improved selectivity, simultaneously.

In this study, heterojunctions of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and BiOI with varying molar ratios (12.5%, 17%, and 25%) were synthesized for use in the photocatalytic

conversion of veratryl alcohol into the corresponding aldehyde under simulated sunlight, achieving complete conversion rates with approximately 95% selectivity.

Material and Methods

The synthesis of the various heterojunctions was carried out by combining the hydrothermal method with co-precipitation. The materials underwent characterization using different analytical techniques including X-ray diffraction (XRD), UV-Vis spectroscopy, nitrogen physisorption, high-resolution transmission electron microscopy (HRTEM), and electrochemical tests. Photocatalytic activity assessments were conducted in 50 mL batch reactors containing 20 ppm of substrate (veratryl alcohol) and a catalyst loading of 0.5 g/L, utilizing simulated sunlight as the light source. The concentrations of both the substrate and the product (veratraldehyde) were determined using reverse-phase HPLC (high-performance liquid chromatography).

To investigate the impact of band structure modulation on photocatalyst reactivity, inhibitor tests were conducted during veratryl alcohol oxidation, along with spin trapping experiments using electron paramagnetic resonance (EPR) spectroscopy with the DMPO nitronyl probe.

Results and Discussion

The findings showed that the photocatalytic activity for veratryl alcohol oxidation to veratraldehyde was significantly enhanced in the heterojunction photocatalysts compared to individual semiconductors. Conversions were observed to be 4 to 20 times higher with the heterojunctions than with $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and BiOI alone, respectively. Moreover, near 100% selectivity was achieved exclusively with the heterojunctions. Among them, the photocatalyst incorporating 12.5% BiOI demonstrated the best combination of performance ($195.2 \mu\text{mol gcat}^{-1}$) and selectivity (93%) compared to unmodified $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (63% selectivity and $36.2 \mu\text{mol gcat}^{-1}$).

These significant enhancements were attributed to the formation of the heterojunction with a pn-type charge transfer mechanism, which greatly increased charge separation and modulated band structure. This, in turn, affected redox potentials and system reactivity, favoring direct substrate oxidation. Inhibitor tests confirmed that the active species involved in oxidation were h^+ (holes) and e^- (electrons), supported by EPR (electron paramagnetic resonance) evidence showing suppressed hydroxyl and superoxide radical production due to the heterojunction. Direct

oxidation on the surface via h^+ occurred, with the veratryl alcohol cation radical identified as a key intermediate in the selective oxidation process, as illustrated in Figure 1.

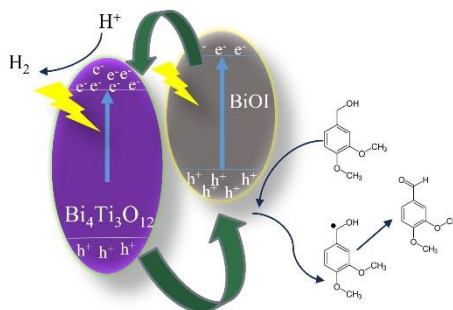


Figure 1. Proposal of the reaction path

Conclusions

The study of the photocatalytic mechanism revealed that the substantial improvement in catalytic performance is attributed to the formation of the heterojunction, enhancing both charge separation and band structure modulation, while also enhancing reactivity, promoting direct substrate oxidation without the mediation of highly reactive oxygen species with high efficiency and selectivity.

Acknowledgments

The authors thank to National Agency for Research and Development (ANID) for financial support by Fondecyt Regular 1201895. J.C. Murillo-Sierra acknowledges the National Agency for Research and Development (ANID) for the financial support through project Fondecyt postdoctoral 3220016.

References

- [1] M. Bellardita, S. Yurdakal, B.S. Tek, C. Degirmenci, G. Palmisano, V. Loddo, L. Palmisano, J. Soria, J. Sanz, V. Augugliaro, *Journal of Environmental Chemical Engineering*, 9 (2021) 105308.
- [2] S. Tu, H. Huang, T. Zhang, Y. Zhang, *Applied Catalysis B*, 217 (2019) 550.
- [3] C. Zhang, W. Fei, H. Wang, N. Li, D. Chen, Q. Xu, H. Li, J. He, J. Lu, *Journal of Hazardous Materials*, 399 (2020) 123109.