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SUMMARY

博士の専攻分野の名称 博士（工学） 氏名 松尾 稜介

学 位 論 文 題 名

Title of dissertation submitted for the degree

Valuable Products Synthesis by Inorganic-Biological Hybrid Microbial-photoelectrochemical Cells

（無機-生物ハイブリッド微生物光電気化学セルによる有価物合成）

There is an urgent need to create a decarbonized society, making it desirable to develop a valuable product synthesis system that utilizes atmospheric CO₂ as a carbon source and renewable energy. Photocatalysts are excited by light irradiation, producing electrical charges ($e^- + h^+$), which drive proton reduction and water oxidation (water splitting). Therefore, photocatalysts can generate hydrogen and oxygen using light energy. Photoelectrochemical (PEC) cells with photocatalysts as electrodes enable water splitting and hydrogen production at the anode and cathode, respectively. This system's advantage is that it allows for the separate production of hydrogen and oxygen. In addition, acetogenic bacteria can synthesize acetate from hydrogen (H_2 , $H^+ + e^-$) and CO₂, which can be used as a raw material for a variety of chemicals. The use of microorganisms as catalysts for carbon dioxide reduction is a promising option because of the advantages of high selectivity, production of complex organics, and the possibility of long-term and large-scale operation due to its self-replication nature. Therefore, acetogenic bacteria are expected to be biocatalysts for the synthesis of carbon dioxide-reducing valuables. Semi-artificial photosynthetic systems integrating photocatalysts and biocatalysts are attracting attention as a new technology capable of synthesizing valuable products from light, water, and CO₂.

The semi-artificial photosynthesis has the following problems:

1. The redox potential of the anode reaction (water splitting) is as high as 0.82 V vs. normal hydrogen electrode (NHE), and the potential difference with the cathode reaction (hydrogen production) is 1.23 V. This potential difference limits the photocatalytic materials that can be used. In addition, an external power supply may be required to supply energy. Furthermore, water splitting requires pure water and consumes energy and cost.
2. Acetogenic bacteria are strict anaerobic bacteria. If oxygen from the anode reaction diffuses into the cathode chamber, it may inhibit the activity of the acetogenic bacteria, making it hard to maintain stable operation. In addition, hydrogen production

competes with the oxygen reduction reaction, reducing the efficiency of the overall system.

This study considers that it is effective to change the anode reaction from water splitting to organic matter oxidation for the above issues. Electroactive bacteria need to be inoculated on the anodes for organic matter oxidation. The redox potential of organic matter oxidation is around $-0.29 \sim -0.43$ V vs. NHE, which can reduce the potential difference with the cathodic reaction by more than 90%. In addition, by changing the electron donor from water to organic matter, pure water can be substituted by wastewater. Furthermore, oxygen is not produced in the organic decomposition reaction, which may prevent the diffusion of oxygen from the anode reaction into the cathode chamber.

This study aimed to construct a CO₂-reduced valuable product synthesis microbial-photoelectrochemical (M-PEC) cell consisting of a bio-photoanode for organic matter oxidation and a cathode that supplies hydrogen to acetogenic bacteria. First, a photocatalyst was fabricated, and PEC performance was evaluated. Then, it was verified whether stable operation of the microbial electrosynthesis (MES) with acetogenic bacteria could be achieved by changing the anode reaction from water splitting to organic matter oxidation. Finally, a bio-photoanode was constructed to examine whether hydrogen production at the cathode could provide a reducing equivalent for the acetogenic bacteria.

This dissertation consists of six chapters as follows:

Chapter 1 provides an introduction to the study, presenting the research background, objectives, and structure of this thesis.

Chapter 2 organizes the report on the synthesis of valuable substances by M-PEC cells, which is the subject of this study, and provides basic information on the related technologies, namely photocatalysis and MES.

In Chapter 3, the photocatalytic electrode ZnO/CuO nanoforests (NFRs) was prepared by thermal oxidation and galvanic submerged photosynthesis of crystallites (G-SPSC). In the fabrication, the effects of sputtering, which is a pre-treatment for G-SPSC, and the UV irradiation time during G-SPSC on the PEC performance were evaluated. In addition, the applicability to M-PEC cells was evaluated. Throughout this chapter, the PEC hydrogen generation ability of ZnO/CuO NFRs was quantified. In addition, the biocompatibility of ZnO/CuO NFRs was evaluated.

In Chapter 4, the anodic reaction was changed from water splitting to organic matter oxidation by inoculating *Shewanella oneidensis* MR-1 to the anode chamber for stable operation of MES with the acetogenic bacteria *Sporomusa ovata*. Throughout this chapter, the effect of anode reaction changing on the activity of *S. ovata* was evaluated.

In Chapter 5, a bio-photoanode integrating ZnO/CuO NFRs and *S. oneidensis*

MR-1 was constructed. The ZnO/CuO NFRs surface was modified to improve the stability and biocompatibility of the ZnO/CuO NFRs. An M-PEC cell consisting of a bio-photoanode and a Pt cathode was constructed to evaluate the effect of light irradiation and *S. oneidensis* MR-1 inoculation on hydrogen production.

Chapter 6 provides a summary of this study and future perspectives.