学　位　論　文　内　容　の　要　旨

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学　位　論　文　題　名

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)

Photocatalysts are excited by light irradiation and produce electrical charges ($e^- + h^+$). These charges are responsible for the reduction of proton reduction and the oxidation of water (water splitting), respectively. 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. Acetogenic bacteria can synthesize acetate from hydrogen (H_2, $H^+ + e^-$) and CO_2, 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 due to 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 CO_2-reduced valuable products. Semi-artificial photosynthetic systems integrating photocatalysts and acetogenic bacteria are attracting attention as a new technology capable of synthesizing valuable products from light, water, and CO_2.

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. Such a large potential difference limits the photocatalytic materials that can be used. In addition, an external power supply may be required. Furthermore, water splitting requires pure water and consumes energy.

2. Acetogenic bacteria are absolutely anaerobic bacteria. If oxygen from the anode reaction diffuses into the cathode chamber, it may inhibit the activity of the acetogenic bacteria, making it difficult to maintain stable operation. In addition, hydrogen production competes with the oxygen reduction reaction, reducing the efficiency of the overall system.

To address the above issues, this study considers it effective to change the anode reaction from water splitting to organic matter oxidation. Exoelectrogen must be inoculated on the anodes to carry out organic matter oxidation. The redox potential of organic matter oxidation is around -0.29 ~ -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 matter oxidation reaction, which may prevent oxygen diffusion from the anode to the cathode chamber.

Here, this study aimed to construct a CO_2-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 its 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 and examined whether hydrogen production at the cathode could provide a reducing equivalent to 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 products 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 photocatalytic electrode performance were evaluated. The applicability of ZnO/CuO NFRs to M-PEC cells was also 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*, and its impact was evaluated.

In Chapter 5, a bio-photoanode integrating ZnO/CuO NFRs and *S. oneidensis* MR-1 was constructed. Surface CuO nanoparticles and thin layers were constructed 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 on hydrogen production.

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