# 論文 / 著書情報
# Article / Book Information

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| 題目(和文) | 高選択的二酸化炭素光還元に向けた助触媒の開発 |
| Title(English) | Development of Co-catalyst for Selective Photocatalytic CO2 Reduction. |
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| 出典(和文) | 学位:博士(学術),<br>学位授与機関:東京工業大学,<br>報告番号:甲第10675号,<br>授与年月日:2017年9月20日,<br>学位の種別:課程博士,<br>審査員:宮内 雅浩,中島 章,日野出 洋文,松下 伸広,松下 祥子 |
| Citation(English) | Degree:Doctor (Academic),<br>Conferring organization: Tokyo Institute of Technology,<br>Report number:甲第10675号,<br>Conferred date:2017/9/20,<br>Degree Type:Course doctor,<br>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

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| 専攻：<br>Department of | 材料工学　　　　専攻 | 申請学位（専攻分野）：<br>Academic Degree Requested | 博士<br>Doctor of　（　学術　　　） |
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）


The photocatalytic carbon dioxide ($CO_2$) reduction has been paid more and more attention owing to its advantage of decreasing $CO_2$ using renewable energies and converting to organic molecules directly. Commonly, the photocatalytic $CO_2$ reduction is achieved by the combination of light harvester and co-catalyst. A light harvester adsorbs solar energy and provides photoexcited electrons and holes, while a co-catalyst provides efficient reaction sites and controls the product selectivity. This thesis reports the development of the co-catalyst of photocatalytic $CO_2$ reduction. Two kinds of co-catalysts, *i. e.* the $Cu_xO$ nanoclusters and the Cu-Zn alloy (electrodes and nanoparticles) were developed. By using Cu-Zn alloy, highly selective HCOOH generation from $CO_2$ reduction was achieved, following with the discussion on the reaction pathways of $CO_2$ reduction. Further, by combining the Cu-Zn alloy co-catalyst with a Z-Scheme system, I achieved photocatalytic $CO_2$ into HCOOH under visible light irradiation, which would be the first report about highly selective $CO_2$ reduction under visible light without sacrificial agent based on robust and inorganic materials.

*Chapter 1* introduced the mechanism and difficulties of photocatalytic $CO_2$ reduction. The objective and strategy of this research were clarified. Based on the previously reported literatures survey, I explained that the development of co-catalyst was found to be highly needed, thus my research was decided to focus on the development of highly selective and robust co-catalyst.

In *Chapter 2,* the $Cu_xO$ nanocluster was successfully prepared by impregnation method and it showed good catalytic properties for $CO_2$ reduction under electrochemical bias application. Further, the $Nb_3O_8^-$ nanosheet was developed as a light harvester for photocatalytic $CO_2$ reduction. The $Cu_xO$ nanocluster grafted $Nb_3O_8^-$ nanosheets converted $CO_2$ into CO under UV irradiation. To clarify the charge transfer and the origin of the chemical products, electron spin resonance (ESR) and isotope trace analyses were investigated, and the reaction mechanism of the present system was discussed.

To improve the activity and selectivity of the co-catalyst, a Cu-Zn alloy electrode was developed in *Chapter 3*. It was prepared by a vacuum sealing method and the composition was characterized as $Cu_5Zn_8$ intermetallic. The electrochemical evaluation proved that the Cu-Zn electrode could convert $CO_2$ into HCOOH with Faradic efficiency of 79 %. When the Cu-Zn electrode was used as the cathode in a photoelectrochemical cell and $SrTiO_3$ electrode was used as a photoanode under UV light irradiation, $CO_2$ was selectively reduced into HCOOH in the cathodic side without any bias-potential. The Faradic efficiency for HCOOH generation was over 70 % and the turnover number for $CO_2$ reduction was as high as 1458. These results reveal high selectivity and stability of my Cu-Zn alloy electrode.

To understand the reason for the high selectivity of the Cu-Zn alloy, the reaction mechanism was studied in *Chapter 4*. According to previous literatures survey, the reaction pathways and their relationship with the co-catalyst surface condition were summarized. In addition, I evaluated *in-situ* FTIR analyses on Cu-Zn NPs loaded STO powder in moist $CO_2$ atmosphere and in moist argon (Ar) atmosphere, then the active species of HCOOH as bidendate $CO_2^-$ radical species were detected on the surface of Cu-Zn alloy, which clearly explained the high selectivity of my catalyst.

To make the Cu-Zn catalyst more generally used, in *Chapter 5*, Cu-Zn alloy nanoparticles were also prepared by chemical co-reduction method, which can easily synthesize different kinds of alloy nanoparticles with different compositions. $Cu_5Zn_8$ NPs were successfully synthesized and their high selectivity for HCOOH generation were reconfirmed by electrochemical evaluation. Further, using an ink method, the Cu-Zn NPs can be easily loaded onto the surface of light harvester under moderate conditions.

*Chapter 6* reported the development of highly selective visible-light-driven $CO_2$ reduction. Even though a Cu-Zn NPs co-catalyst was successfully developed and proved to behave highly activity in the previous chapters, it's still difficult to achieve visible light driven $CO_2$ reduction because of the cogent requirements for the light harvester system. The light harvester should provide high conduction band position and deep valence band position to catalyze both the $CO_2$ reduction

and water oxidation reactions. Also, it is required to be visible light responsive to expand the range of absorbed solar energy. However, these two requirements are very hard to be satisfied simultaneously because of the trade-off relationship between the high band position and narrow bandgap value. To solve this problem, a Z-scheme system, which is constructed by visible-light-sensitive $CaFe_2O_4$ (CFO) photocathode and $WO_3$ nanotree photoanode, has been developed in the present chapter. By decorating the surface of CFO using Cu-Zn NPs, the photocatalytic performance for $CO_2$ reduction increased significantly. HCOOH was generated as main product and water was confirmed to be the electron donor to produce oxygen. Compared to the previous researches, this work should be significantly impact in the field of photocatalysis, because of not only achieving visible light photocatalytic $CO_2$ reduction without sacrificial agents but also showing outstanding selectivity for HCOOH generation. The present study is the first report to achieve more than 50 % selective $CO_2$ reduction under visible light irradiation through water oxidation. Besides, the light-to-energy conversion efficiency reaches 0.028 %, which is much higher than the previous reports.

In *Chapter 7*, the strategy to achieve highly selective co-catalyst design was presented, based on tuning the surface adsorption strength for the active species during the reaction pathway. The present findings can be generally used in various catalytic areas, to stimulate the researchers on wide variety of co-catalysts design and development not only for $CO_2$ reduction but also other reactions involving multi-electron process.

At last, *Chapter 8* summarizes this thesis.