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Title	Study of Photoelectrochemical CO ₂ Reduction by Designing Novel Metal Cathodes and Semiconductor Photoanodes with Functional Nanostructure [an abstract of dissertation and a summary of dissertation review]
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Degree Grantor	北海道大学
Degree Name	博士(理学)
Dissertation Number	甲第12377号
Issue Date	2016-06-30
Doc URL	https://hdl.handle.net/2115/62453
Rights(URL)	https://creativecommons.org/licenses/by-nc-sa/2.1/jp/
Type	doctoral thesis
File Information	Li_Mu_abstract.pdf, 論文内容の要旨



学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称

博士（理学）

氏名 李 牧

学 位 論 文 題 名

Study of Photoelectrochemical CO₂ Reduction by Designing Novel Metal Cathodes and Semiconductor Photoanodes with Functional Nanostructure

(新規ナノ構造電極の構築およびCO₂の光電気化学還元に関する研究)

Due to the increasing worldwide demand for fossil fuels and the accompanying excessive emissions of greenhouse gas carbon dioxide, finding a highly efficient, selective and economical approach toward carbon dioxide conversion becomes a great challenge in realizing an artificial system for sustainable carbon cycle. The approach of photoelectrochemical (PEC) CO₂ reduction is believed to be one of the most promising candidates for the future-oriented generation of CO₂ recycling technique, since the profound Honda-Fujishima effect has been discovered by the early 1970s. However, so far most of the PEC CO₂ reductions mainly focused on the cathodic half reaction for the directly CO₂ reduction over p-type semiconductor electrodes, such as poisonous phosphides and arsenides. The high overpotentials and limited options of photocathode candidates significantly restrict the research of PEC CO₂ conversion. Furthermore, there are still not enough reports about overall PEC CO₂ reduction. In this respect, the main strategy of this thesis is to study overall PEC CO₂ reduction process by constructing a PEC device with metal cathode and n-type semiconductor photoanode. Both of the cathodic and anodic sides were studied, respectively, and finally a PEC device was constructed by integrating these designed electrodes for obtaining a highly efficient, selective and low energy consumption CO₂ conversion.

Chapter 1 gave a general introduction of the PEC CO₂ reduction, the interrelated photocatalytic CO₂ reduction and electrochemical CO₂ reduction process as well as the design strategy of PEC construction for the study in this thesis.

In chapter 2, a photocatalytic reduction of CO₂ over wide band-gap semiconductor NaTaO₃ was investigated as a preliminary study for the following PEC CO₂ reduction. Various noble metal cocatalysts were loaded on NaTaO₃ to investigate their function in determining the activity and selectivity of photocatalytic CO₂ conversion. This study demonstrated that the photocatalytic activities over oxides semiconductor are greatly restricted by the unstable water oxidation. On the other hand, noble metal cocatalysts significantly determined the product selectivity. The accumulation mechanism of peroxides

intermediates was confirmed during the water oxidation process. Introducing electron donor H_2 could effectively overcome this drawback to obtain a stable reactivity. Ru and Pt were found effective as cocatalysts on hydrogen activation, stabilization and utilization in the presence of electron donor during the gaseous photocatalytic CO_2 reduction process. They exhibited superior activities for the selective reduction of CO_2 to CH_4 ($51.8 \mu mol h^{-1} g^{-1}$) and CO ($139.1 \mu mol h^{-1} g^{-1}$), respectively.

In chapter 3, novel mesoporous palladium-copper bimetallic electrocatalysts were studied for achieving an efficient and selective CO_2 reusable performance. It was reserved as the cathodic material within the PEC device. This was the first research by introducing mesoporous alloys as the electrocatalysts for the selective reduction of CO_2 to CO. The optimal ratio was obtained at Pd_7Cu_3 , with Faradic efficiency (FE) for CO exceeding 80% at -0.8 V vs. RHE. The mesoporous nanostructures could provide roughened surfaces with abundant active sites and could promote selective conversion of CO_2 to CO. DFT calculations demonstrated that Pd atoms served as the reactive centers, while Cu could effectively altered the electronic structure and the adsorption ability of its neighbor Pd within the alloys due to the geometric and electronic effects.

Chapter 4 investigated the water oxidation half reaction over photoanode for the overall PEC CO_2 reduction. Hierarchical carbon nanotube (CNT) and Co_3O_4 decorated ZnO nanowire (NW) arrays composites were fabricated for the half reaction of water oxidation. The ZnO NWs served as the main photo-absorber. CNTs, as cocatalysts, promoted the separation and transfer of photogenerated electrons. Co_3O_4 synergistically transferred the holes and against photo-corrosion of ZnO, so that facilitated the water oxidation. It exhibits a photocurrent density ($1.9 mA cm^{-2}$ at 0.6 V vs. Ag/AgCl, 2.7 times larger than pristine ZnO NWs), improved incident photon to current conversion efficiency (52.5% at 340 nm, 5.1 times higher than pristine ZnO NWs) under AM 1.5G simulated sunlight. The heterogeneous ternary architecture with certain functional components was found as an effective approach for fabricating photoanodes.

Finally in chapter 5, an overall PEC CO_2 reduction was investigated by integrating the mesoporous Pd-Cu cathode and ZnO-based NWs photoanode. This was the first research attempt about overall PEC CO_2 reduction by assembling designed metal cathode and semiconductor photoanode with specific nanostructure. It was found that the overall PEC CO_2 conversion activity was an integrated performance and was determined by both of the cathodic and anodic side. The maximum FE_{CO} of the PEC CO_2 reduction is ca. 75% at bias -1.2 V, with incident photon to current conversion efficiency value of 16% at 340 nm. The metal cathode directly determined the CO_2 conversion activity depending on the density of active sites. The photoanode dominated the solar utilization efficiency of the overall PEC CO_2 reduction process.

In summary, this thesis revealed that integrating metal cathode electrocatalysts and n-type photoanode semiconductors provides a promising approach for overall PEC CO_2 reduction. The designed specific nanostructures of both the cathodic and anodic materials played important role on the performance of PEC CO_2 conversion. Moreover, this study opened up a perspective strategy towards obtaining efficient, selective and low energy consumption PEC CO_2 reduction in the future research.