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　パン　ホン

学 位 論 文 題 名

Construction of Semiconductor-based Photosystem for CO_2 Reduction and Water Oxidation towards Artificial Photosynthesis

（人工光合成を目指した半導体光触媒による CO_2 還元および酸素生成に関する研究）

Mimicking the natural plant, artificial photosynthesis offers a promising strategy to close the carbon cycle on the earth. Involved with the challenging CO_2 fixation over *Photosystem I* and the sluggish water oxidation over *Photosystem II*, the processes do not occur readily. Zinc sulfide (ZnS) and the photosynthetic membrane protein are regarded as the most promising catalysts for CO_2 reduction reaction (CO_2RR) and oxygen evolution reaction (OER) for their negative conduction band and high turnover frequency (TOF), respectively. However, previous efforts have demonstrated the superior CO_2RR activity of colloidal ZnS nanocrystals and the OER activity of *Photosystem II* but their performance is limited by light absorption. Furthermore, the active sites and reaction mechanism are worth deep understanding for future materials design. Thus, this thesis focused on constructing half reactions of CO_2RR and OER using visible-light responsive photocatalysts with an emphasis on the active site-regulated CO_2RR process.

In chapter 1, an overview of artificial photosynthesis and the semiconductor-based photocatalysis are introduced. The general principle for designing the photocatalysts for CO_2RR and OER are given. The chapter also briefly summarized the development and application of zinc sulfides in hydrogen evolution reaction (HER) and CO_2RR in the past years. Several commonly used strategies for constructing efficient CO_2RR and the Photosystem II-based systems are also briefly reviewed.

In chapter 2, well-designed colloidal Cu-doped ZnS (ZnS:Cu) nanocrystals were synthesized and operated as a promising visible-light-responsive photocatalyst in all-inorganic reaction system. Two functional elements, Cu and Cd, are respectively used as dopant and cocatalyst of ZnS nanocrystal for selective CO_2 reduction. Cu doping expands the photoabsorption of ZnS into visible light region and the simultaneous Cd^{2+} surface modification significantly improves the activity of CO_2RR with 99% formic acid selectivity.

In chapter 3, aqueous colloidal Ni-doped ZnS (ZnS:Ni) nanocrystals were constructed as another excellent photocatalyst for CO_2RR into formate under solar light irradiation and as a case study to investigate the interplay between Ni doping and sulfur vacancies. It is revealed that the abundant sulfur vacancies and extended visible light absorption of the constructed colloidal ZnS:Ni nanocrystals contribute to the prominent performance for CO_2RR; excessive doping of Ni does not guarantee an increase of photocatalytic CO_2RR due to a diminish of sulfur vacancies.

In chapter 4, the mechanism by which the colloidal ZnS nanocrystals loaded with Cd^{2+} induced a remarkable enhancement in the selective production of formate was investigated. We present the spectroscopic evidence of the Cd status using the X-ray absorption fine structure (XAFS) and electron behaviors associated with sulfur vacancies, deep dopants and surface Cd sites by photoluminescence (PL) spectroscopy and transient absorption spectroscopy (TAS). Ab initio calculations reveal that a higher density of states near band-edge from Cd s orbital accounts for the favorable charge transfer

and disclose the pathways during CO_2 activation and reduction, together with the *in situ* attenuated total reflectance-infrared (ATR-IR) spectroscopic observation.

In chapter 5, cation vacancy-rich ZnS was constructed to create Zn vacancies (V_{Zn}) as active sites instead of the anion vacancies for CO_2RR on the surface while reserving the charge transport capability in the bulk. With no co-catalyst, the ZnS acquired a high selectivity of formate production ($> 85\%$).In situ attenuated total reflection-infrared (ATR-IR) spectroscopy and first-principle calculations have been used to elucidate the pathways of CO_2RR into formate and prove the surface V_{Zn} as favorable active sites by greatly lowering the barrier of the CO_2RR process and precluding the proton adsorption, clarifying the origin of the highly selective CO_2RR into formate in the presence of competitive hydrogen evolution reaction (HER).

In chapter 6, a bio-hybrid photoanode of a photosynthetic membrane protein (Photosystem II), the exclusive photosynthetic complex responsible for OER were fabricated on mesoporous WO_3lm for water oxidation. The Photosystem II membrane proteins have been communicated with the WO_3 electrode in the absence of any soluble redox mediators and sacrificial reagent under the solar spectrum even to 700 nm and a maximum incident photon-to-current conversion efficiency (IPCE) reaches 15.24% at 400 nm. This work represents a preliminary effort towards construction of the monoclinic artificial photosynthetic leaf.

In chapter 7, an overall summary and the future prospects of this dissertation work are presented. This thesis carried out a systematic study on the half reactions of CO_2RR and OER over "Photosystem I" and "Photosystem II" , respectively. Doping effect, surface vacancies and isolated co-catalyst are demonstrated of great significance on the photocatalytic CO_2RR activity over ZnS photocatalyst; their impacts are disclosed experimentally and theoretically, deepening the understanding of the CO_2RR pathways. Initial efforts on OER are also paid on constructing *Photosystem II*|mesoporous WO_3 film as the other segment of one monoclinic artificial leaf. This study potentially provides new inspirations for facile synthesis and rational design of more efficient photocatalysts towards artificial synthesis in the future research.