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　　ワンチィ

学 位 論 文 題 名

Construction and Modification of Ternary Metal Sulfide for Efficient Photocatalytic CO_2 Reduction
（三元系金属硫化物の組成および表面構造制御による効率的な光触媒 CO_2 還元に関する研究）

Photocatalytic carbon dioxide reduction is one of the most promising strategies to solve the energy crisis and achieve the global carbon cycle. Developing and designing highly efficient photocatalysts for photocatalytic CO_2 reduction under visible light has become a hot topic over the world. Metal sulfide-based materials have been widely used in photocatalytic CO_2 reduction due to their low cost, high stability, and suitable band structure. However, the metal sulfide photocatalysts still suffer obvious drawbacks, such as high photogenerated electron-hole pairs recombination rate, less reactive sites, and so on. To overcome these drawbacks, two fundamental strategies can be considered: the construction of suitable electronic structures and abundant reaction sites. Therefore, this thesis focuses on the rational design of metal sulfide photocatalysts with appropriate electronic structures by modifying the elemental ratio and constructing more reactive sites on the catalyst surface through surface engineering.

In chapter 1, a general background about semiconductor-based photocatalytic CO_2 reduction and the concept of photocatalysts were introduced. Then, the key factors and common strategies for enhancing photocatalytic activity were discussed. In the end, the ongoing research beyond ternary metal sulfide was summarized.

In chapter 2, the facile fabrication of Cd-In-S (CIS) colloidal nanocrystals was constructed as an efficient visible light-responsive photocatalyst for the conversion of CO_2 to CO. Both experimental and theoretical investigations reveal the importance of Cd to In ratio, which positively influences not only the charge carrier separation rate but also the electronic structures of the CIS samples. In particular, the light absorption ability, redox potential of photo-induced electrons, and charge transfer ability from CIS to the cobalt-based cocatalyst were effectively modulated, endowing the optimized sample with a high CO evolution rate of 22.9 μmol h^{-1} and selectivity up to 80% under visible light irradiation. This work's findings provide guidance for designing and constructing ternary metal sulfide materials for CO_2 conversion by modulating elemental ratio.

In chapter 3, the non-stoichiometric Ag-In-S quantum dots (QDs) was constructed as highly efficient and robust photocatalysts for visible-light-driven photocatalytic reduction of CO_2 to syngas at atmospheric pressure and room temperature. The introduction of $Co(bpy)_3^{2+}$ (bpy = 2'2-bipyridine) cocatalyst can promote the conversion of CO_2 to CO reaction and meanwhile improve the photo-stability of Ag-In-S QDs. The photocatalytic activity and selectivity of Ag-In-S QDs are strongly dependent on the Ag to In molar ratios, and the optimized sample exhibits the highest CO evolution rate of 9.20 μmol $h^{-1,}$ and H_2 evolution rate of 3.13 μmol h^{-1}, corresponding to the CO selectivity of 74.61%, outperforming most of the reported QDs based photocatalysts. This work provides a new example of Cd and Pb free QDs photocatalysts for efficient and stable CO_2 photoreduction.

In chapter 4, a $CdS_{0.8}CdSe_{0.2}$ colloidal quantum dot was prepared by a simple method as an excellent visible light reactive photocatalyst for the reduction of CO_2 to carbon monoxide. In addition, vacancy defects were created on the quantum dot surface by a simple acidic solution etching method to enhance the photocatalytic carbon dioxide reduction activity. The optimal sample exhibited the highest CO production rate of 19.79 μmol h^{-1} and selectivity of up to 77%. It can be demonstrated that the surface vacancy defects contribute to the outstanding performance of photocatalytic CO_2 reduction. In this paper, the role of the introduction of Cd vacancies in the photocatalytic CO_2 reduction activity is presented and discussed. This work provides guidance and theoretical insight for vacancy construction on QDs for potential photocatalytic CO_2 reduction.

In chapter 5, an overall summary of this dissertation work was presented. This thesis presents a systematic study on the elemental ratio modification of metal sulfides and their surface defects construction for efficient photocatalytic CO_2 reduction. By adjusting the proportion of metal elements in the ternary metal sulfide, the electronic structure of the catalyst can be effectively tuned, which is an effective way to improve photocatalytic performance. The construction of more reactive sites on the catalyst surface by surface etching can directly affect surface catalysis. The relevant findings of this study deepen the understanding of metal sulfide photocatalysts for CO_2 reduction.