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 雲祥

学 位 論 文 題 名

Structure Engineering of Carbon-based Materials for Efficient Photocatalysis

（高効率光触媒の構築に向けた炭素系材料の構造制御に関する研究）

Metal free carbon-based materials, featuring low cost, editable structure and unique physicochemical property, are promising candidates for photocatalytic systems. Among them, polymeric carbon nitride (CN) has attracted extensive attention as photocatalyst in recent years due to its low cost, ease of synthesis, and appropriate band structure. However, efficient solar-to-energy conversion over CN still encounters great challenges because of its inherent drawbacks, such as the fast recombination of photocarriers, poor electronic conductivity. Furthermore, the lack of robust active sites on carbon co-catalysts and interfacial contamination with adventitious carbon severely limit the overall photocatalytic efficiency of carbon-based photocatalytic systems. In this work, the object is to design and develop carbon-based materials via modulating the intrinsic properties of photocatalyst CN, creating novel carbon-based co-catalyst and removing the relevant interfacial adventitious carbon for efficient photochemical processes and thus to further understandings of carbon-based materials as well as the corresponding mechanism of photocatalysis.

In chapter 1, an overview of photocatalysis was introduced first. Then, a review of photocatalytic system, including the photocatalysts, co-catalysts, interfaces and relevant modulation strategies, was given. In the end, the recent development of carbon-based photocatalytic system was summarized.

In chapter 2, to improve the poor electronic conductivity of CN and thus to promote the charge carrier separation and transfer behavior, a conceptual and facile strategy was developed to construct carbon chains incorporated CN. Various kinds of carbon chains can connect the in-plane defects of CN via strong covalent C-N bonds. Those embedded atomic carbon chains could efficiently mediate the electron transfer in the basal plane of CN. As a result, the optimal carbon chains-planted CN delivers a remarkably enhanced photocatalytic performance, achieving a 13.2 and 29.2-fold improvement in H_2 evolution and CO_2 reduction, respectively. This study provides an in-depth insight into the modulation of in-plane electrical conductivity at molecular scale over CN and offers new opportunities for reinforcing the reaction kinetics of organic-based photocatalysts.

In chapter 3, a facile, green, and reversible exfoliation-reassembly strategy was developed to switch the features of polymeric CN for different photoredox reactions. The OH groups are implanted between the layers of CN in advance, then the introduced small-sized protons enter into the layer spacing and neutralize the OH to produce H_2O. The giant expansion effect of in situ-generated H_2O molecules confined to the interlayer results in the mass production of ultrathin

polymeric CN nanosheets, giving a high yield, i.e., up to 48%, of ultrathin nanosheets in a mild solution (pH ~1.3). Interestingly, the exfoliation-reassembly process, as well as the properties of CN are largely reversible via alternating the interlayer groups. Moreover, the exfoliated and reassembled CN achieve a superior photocatalytic activity for *iso*-propanol (IPA) degradation (acetone: 345 μmol/h; CO_2: 23 μmol/h) and H_2 evolution (1370 μmol/h), resulting in a high apparent quantum yield (AQY) of 27% and 46%, respectively, at ~420 nm. This new proof-of-concept strategy will open up further opportunities for more effective delamination of extensive layered 2D materials towards advanced applications.

In chapter 4, a robust single cobalt co-catalyst Co-NC (with isolated $Co-N_4$ moieties on N-rich carbon sheets) was fabricated and anchored on photoharverster CdS. Subsequently, the interfacial adventitious carbon between CdS and Co-NC was targetedly removed by a facile annealing process, resulting in a cleared interface with small resistance. It's found that surface-trapped electrons can readily migrate to the firmly attached Co-NC across the cleared interface between CdS and Co-NC. The small-resistance interfacial carrier path and the robust single-cobalt sites work in a cooperative way and hence achieve a superior visible-light-driven H_2 generation activity with a rate of 4.34 mmol/h, an apparent quantum yield (AQY) of 63.9 % at 400 nm and a ultrahigh turnover frequency (TOF) of up to 16714.7 h^{-1}. This finding will motivate future work in creating clean interfaces and unique single active sites for high-performance photocatalysis.

In chapter 5, an overall summary of this dissertation work was presented. This thesis carried out a systematic study on the construction of efficient carbon-based materials for visible-light-driven photocatalytic reactions, including H_2 evolution, CO_2 reduction, and isopropanol (IPA) degradation. This thesis reveals that the structure engineering carbon-based materials and relevant interfaces are of significance to improve photocatalytic activity. Furthermore, the findings in this study also deepen the understanding of carbon-based photocatalytic systems, shed light on the mechanism of photocatalysis, and importantly, highlight some universal design strategies for efficient photochemistry processes.