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学 位 論 文 題 名

Structural and Environmental Modulation on Graphitic Carbon Nitride Materials for Efficient Photocatalytic Hydrogen Evolution

(構造及び反応場を制御したカーボンナイトライド光触媒による水素生成に関する研究)

Photocatalytic H_2 evolution represents a promising technology for solar energy conversion and storage and therefore attracts enormous interest. Among various photocatalysts, graphitic carbon nitride ($g-C_3N_4$) has recently emerged as an attractive photocatalyst for H_2 production because of its unique properties, including suitable energy band structure for water reduction, high chemical and thermal stability, and cost effective metal-free composition. However, due to insufficient light absorption, fast electron-hole recombination and kinetic limitation in proton reduction, the photocatalytic performance of $g-C_3N_4$ for H_2 evolution still remains moderate. In this work, the object is to design and develop $g-C_3N_4$ -based materials via structure engineering and reaction environment modulation towards superior photocatalytic activity for H_2 evolution and thus to further the understanding of $g-C_3N_4$ -based materials as well as the corresponding mechanism of photocatalysis.

In chapter 1, an overview of photocatalysis, including photocatalytic water splitting, photocatalytic pollutant degradation and CO_2 photoreduction, was introduced firstly. As followed, a review of strategies to modify photocatalysts for more efficient photocatalysis was also given. At the end, the photocatalysis of $g-C_3N_4$ -based materials was summarized.

In chapter 2, to extend the light absorption and to improve the carrier separation and transfer, the defect-modified $g-C_3N_4$ (DCN) was prepared by a $NaBH_4$ treatment at low temperatures ($< 350\text{ }^{\circ}C$) in an Ar atmosphere. It was found that the resultant DCN not only showed much red-shifted absorption edges, but also exhibited both n- and p-type conductivities due to the implantation of cyano terminal $C\equiv N$ electron-acceptor groups, resulting in the generation of p-n homojunctions. Such homojunction structured DCN photocatalysts were demonstrated to highly efficient in the transfer and separation of photoexcited carriers and consequently presented much enhanced photocatalytic H_2 evolution activity under visible-light. The findings provide an insight into the defect-related issues of $g-C_3N_4$ materials and might represent a promising route for the rational design of photocatalysts with unique architectures for more efficient solar

energy conversion.

In chapter 3, considering the atomic order degree in solid-state materials is crucial for the efficient separation and transfer of photogenerated charge carriers, g-C₃N₄ with improved in-plane ordering was prepared via a spatially confined poly-condensation process using self-assembled heptazine hydrate as the precursor. It was shown that the improved in-plane ordering rendered the as-prepared g-C₃N₄ much increased electron delocalization within the π -conjugated aromatic rings and meanwhile highly improved carrier separation and transfer. As a result, such material exhibited a high hydrogen evolution rate of 420 $\mu\text{mol/h}$ with an apparent quantum efficiency of 8.9% at 420 nm, which was about 14 times higher than that of reference g-C₃N₄ (prepared without structure modulation). These findings emphasized the significance of the molecular ranging regularity of g-C₃N₄ for the efficient photocatalysis.

In chapter 4, a natural photosystem inspired phosphate environmental (precisely, HPO_4^{2-} ions) modulation was further explored to improve the photocatalytic H₂ production over g-C₃N₄ nanosheets under visible light irradiation. With the optimal addition of HPO_4^{2-} , a H₂ evolution rate as high as 947 $\mu\text{mol h}^{-1}$ was achieved for g-C₃N₄ nanosheets (with the apparent quantum yield of 26.1% at 420 ± 14.5 nm) which was about 16 times higher over that of bulk g-C₃N₄. Evidenced by photoelectrocatalytic analysis and theoretical calculations, such significant improvement in H₂ production relied on the synergy of enhanced proton reduction and improved hole oxidation. More importantly, the phosphate was confirmed to indeed play roles resembling those in natural photosynthesis: as a proton pump to facilitate the proton transfer in reaction solutions, and as a mediator that participates directly in proton reduction, thus leading to a Calvin-cycle-like H₂-evolution pathway.

In chapter 5, an overall summary of this dissertation work was provided. This thesis revealed that, the structure engineering and reaction environment modulation on g-C₃N₄ are of significance to improve its activity for photocatalytic H₂ evolution, which not only effectively affect the intrinsic properties of g-C₃N₄ (such as band structure, electronic configuration), but also cast profound impacts on the photocatalytic H₂ evolution pathway. Furthermore, the findings in the study deepen the understanding of g-C₃N₄-based materials, aid to shed light on the mechanism of photocatalysis and importantly, highlight some universal design principles to efficient photocatalysis