Engineering Photocatalysts towards High-Performance Solar Hydrogen Production

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Abstract

The production of chemical fuels by solar energy conversion is regarded as one of the major strategies to address the aggravating energy and environmental problems. Particularly, photocatalytic water splitting has attracted tremendous attention since it represents a clean, cost-effective and environmental-benign technique for solar hydrogen (H_2) production. The core challenge of this promising technology lies in the development of low-cost and environmentally-friendly photocatalyst/co-catalyst systems with high activity and stability. However, to date most of the photocatalysts and co-catalysts are based on transitional metals and noble metals (*e.g.* Pt), respectively, which are neither economic nor environmental-benign. Therefore, the development of metal-free photocatalysts and noble-metal-free co-catalysts are highly desirable. This thesis aims to design and fabricate different highly-active and stable metal-free photocatalyst and noble-metal-free co-catalyst to achieve high-efficient solar H_2 production.

The first part of this thesis focuses on developing high-performance and low-priced metal-free graphitic carbon nitride (g-C_3N_4) photocatalysts as an alternative to current metal-based photocatalysts. Porous P-doped g-C_3N_4 nanosheets (PCN-S) were firstly synthesized by combining P doping and thermal exfoliation strategies. The P-doped conjugated system and novel macroporous nanosheet morphology synergistically contribute to the outstanding photocatalytic H_2-production activity of PCN-S under visible-light irradiation. Furthermore, the P doping was found to create empty midgap states in PCN-S, which greatly extend the light-responsive region; whilst the novel macroporous structure benefits the mass-transfer process and enhances light harvesting. This work not only demonstrates an easy, eco-friendly and scalable strategy to synthesize highly efficient porous g-C_3N_4 nanosheet photocatalysts, but also paves a new avenue for the rational design and synthesis of advanced photocatalysts by harnessing the strong synergistic effects through simultaneously tuning and optimizing the electronic, crystallographic, surface and textural structures.

The second part of this thesis is to design and synthesize a series of earth-abundant co-catalysts for replacing rare and expensive Pt. Ni-based co-catalysts, *e.g.* NiS, metallic Ni and $Ni(OH)_2$, were deposited on $Zn_xCd_{1-x}S$ nano-particles (NPs) to greatly enhance their visible-light photocatalytic H_2-production activity. Particularly, $Ni(OH)_2$ loaded $Zn_xCd_{1-x}S$ shows superior photocatalytic performance to Pt-loaded $Zn_xCd_{1-x}S$ under the identical conditions. This outstanding performance originates from the notable synergetic effect between $Ni(OH)_2$ and metallic Ni formed *in situ* during the photocatalytic reaction. We also for the first time designed and fabricated a novel MXene material, Ti_3C_2 NPs, as a highly-efficient co-catalysts. Ti_3C_2 NPs were rationally incorporated with

CdS by a hydrothermal technique to achieve a super high visible-light photocatalytic H_2-production performance. This remarkable performance results from the optimized Fermi level, efficient hydrogen evolution capacity and novel active sites on Ti_3C_2 NPs. Our work demonstrates the huge potential of earth-abundant MXene family materials to fabricate numerous high-performance and low-cost photocatalysts/photoelectrodes.

The third part of this thesis aims to reveal the superior electron extracting capacity of Ti_3C_2 NPs on $Zn_xCd_{1-x}S$ towards visible-light induced H_2 production. Through combining the experimental techniques and theoretical computations, we have explored the critical role of Ti_3C_2 NPs loaded on the surface of $Zn_xCd_{1-x}S$, which greatly promotes the vectorial electron transfer from $Zn_xCd_{1-x}S$ to Ti_3C_2 NPs. The as-synthesized Ti_3C_2 modified $Zn_xCd_{1-x}S$ composite exhibits the highest photocatalytic H_2-production activity of 7196 $\mu mol\ h^{-1}\ g^{-1}$ at the optimal loading content of 4 wt%. This work demonstrates the possibility of using Ti_3C_2 to replace expensive Pt in photocatalytic H_2 production.