



Title	Construction and Modification of Cobalt Active Sites for Efficient Photocatalytic Hydrogen Generation [an abstract of dissertation and a summary of dissertation review]
Author(s)	レン, シャオファイ
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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 レン シャオフィ

学位論文題名

Construction and Modification of Cobalt Active Sites for Efficient Photocatalytic Hydrogen Generation
(コバルト活性部位の構築と修飾による効率的な光触媒水素生成に関する研究)

Semiconductor-based photocatalysis that directly converts solar energy into hydrogen (H_2) has been recognized as an essential technology in “Green Chemistry”. In a highly efficient photocatalyst system, the utilization of cocatalyst is necessary to boost photogenerated electron-hole pair separation and to provide sufficient active sites for surface chemical reactions. Of particular interest, cobalt and cobalt species have been endowed with competitive advantages over noble metals as the cocatalysts for photocatalytic H_2 generation. However, traditional cobalt-based cocatalysts still encounter great challenges such as low active sites utilization efficiency and poor chemical stability. To overcome the aforementioned drawbacks, it is highly desirable to have rational design on the active sites of cobalt-based cocatalyst. Thus, the object of this thesis is to realize controllable growth and distribution of cobalt-based cocatalysts as well as to modify the cobalt active sites with improved efficiency and stability for photocatalytic H_2 generation. By taking CdS as benchmark semiconductor, the relations between interfacial charge transfer behavior and coordination environment of cobalt active sites have been studied, which can provide basic understanding about the mechanism of modifications over cocatalyst/semiconductor system to achieve high activity.

In chapter 1, a general background about semiconductor-based photocatalytic H_2 generation and the concept of cobalt-based cocatalysts were introduced. Then, the key factors on modifying cobalt active sites toward improved catalytic performance, including loading amount, size effect, and coordination environment were discussed. In the end, the ongoing researches beyond CdS and cobalt-based cocatalysts were summarized.

In chapter 2, in order to maximizing the size effect and enlarging surface exposed area of cobalt-based active sites, two-dimensional black phosphorous (BP) has been chosen as the substrate for dispersing single-atom cobalt active sites. Owing to the intrinsic lone pair electrons, cobalt ions can be stably anchored on the surface of BP nanosheets through Co-P coordination. In-depth structural examination revealed that one isolated Co atom is coordinated with one or two phosphorous atoms as well as four oxygen atoms by forming Co-P(O) species in BP-Co atomic structure. An evidential improvement of photocatalytic reduction capability has been realized due to the interaction between Co and P, while 18-fold enhancement can be achieved on CdS when taking BP-Co as a noble-metal-free cocatalyst for H_2 evolution (the

average H₂ production rate is 345.4 μmol h⁻¹). This strategy can open up new opportunities for constructing atomically active sites in low-dimensional nanostructure.

In chapter 3, a novel and facile preparation strategy has been developed to fabricate ultrafine CoP nanoparticles on the surface of CdS. By utilizing organophosphorus compound triphenylphosphine (PPh₃) as phosphorous source, the as-fabricated CoP nanoparticles were intrinsically encapsulated by carbon layer and applied as cocatalyst into photocatalytic H₂ evolution. This synthesis strategy does not require flammable compounds (e.g. PH₃ or H₂, etc.) or corrosive conditions, which makes it much safer and easier to manipulate comparing to conventional methods. It was found that Ca²⁺ as an alkaline earth metal ion may easily substitute the Cd²⁺ lattice sites of CdS. Specially, intimate contact between CdS and CoP can be realized owing to the ascending reducibility of CdS after Ca²⁺ modification. Meanwhile, the Ca²⁺ dopants can act as surface trapping sites on CdS, leading to strong trap-state emission together with long-lived charge carriers. Benefitted from fast interfacial charge transfer and effective photogenerated electron-hole separation, the photocatalytic H₂ generation rate of Ca-doped CdS-CoP can reach up to the highest value (about 2441.5 μmol h⁻¹ with turnover frequency as high as 703.2 h⁻¹) under optimal conditions. This finding simplifies the fabrication procedure for constructing and modifying cobalt active sites with efficient photocatalytic H₂ generation performance.

In chapter 4, the spatially separated Co and CoO_x dual cocatalyst encapsulated in carbon substrate was constructed by annealing ultrathin two-dimensional (2D) Co-based MOF (Co-MOF) nanosheets on the surface of CdS. The cooperation between Co (reduction cocatalyst) and CoO_x (oxidation cocatalyst and hole acceptor) has been regarded to play an important role for high-efficient photocatalytic H₂ evolution. In addition, the intimate contact between CdS and cobalt active species in carbon matrix that formed after calcination could also enable fast charge transfer for efficient catalytic reactions. As a result, an approximate 12.5-fold enhancement of H₂ generation performance from 0.161 mmol h⁻¹ of CdS to 1.997 mmol h⁻¹ of the newly formed CdS-Co-CoO_x@C with the apparent quantum efficiency of 43.7% at 420 nm has been achieved. The fundamental roles of 2D-MOF derived carbon matrix toward rational construction of dual cobalt active species were visualized by combining a series of in-situ and ex-situ temperature-dependent analytic strategies. This study provides comprehensive understanding on the structural variation of 2D-MOF nanostructure during pyrolysis, offering a meaningful way for controllable designation on dual cobalt-based cocatalyst towards efficient photocatalytic applications.

In chapter 5, an overall summary of this dissertation work was presented. This thesis carried out a systematic study on the construction and modification of cobalt active sites for photocatalytic H₂ generation under visible light irradiation. The thesis reveals that both surface chemistry and electronic properties of cobalt-based cocatalysts can be altered through rational design and modification. Three feasible strategies were found to be crucial for the significant improvement on photocatalytic H₂ generation performance: 1) construction of spatially separated cobalt active sites with optimized structure for improving active sites utilization efficiency; 2) modification of interfacial charge transfer behavior between semiconductor and cocatalyst for promoting photogenerated electron-hole pair separation; and 3) engineering the coordination environment of cobalt active sites for lowering energy barrier in surface reactions. The relevant findings in this study deepen the understanding on rational design of cobalt-based cocatalysts, which provides new insights toward construction and modification of cobalt active sites for photocatalytic H₂ generation.