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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　楊 高梁

学 位 論 文 題 名

Surface/Interface Modulation of Hematite-based Photoanodes for Efficient Photoelectrochemical Water Oxidation

（表面/界面構造制御によるヘマタイト系光電極の効率的な水の酸化反応に関する研究）

Photoelectrochemical (PEC) water splitting is a promising approach for direct conversion of solar energy to hydrogen. Among various semiconductors, hematite (α-Fe_2O_3) has emerged as an excellent photoanode material due to its significant light absorption, chemical stability in aqueous solutions, and earth abundant property. However, its performance has been crucially limited by poor optoelectronic properties and sluggish reaction kinetics for water oxidation. Two essential criteria, including sufficient targeted reaction sites and efficient interfacial charge transfer, should be considered to enhance the performance of hematite-based photoanodes. Thus, this thesis focused on rationally designing efficient co-catalysts with modulated active sites as well as interface engineering by inserting hole transfer mediators/constructing direct chemical interaction between α-Fe_2O_3 and co-catalysts.

In chapter 1, a general background about photoelectrochemistry and a simple overview of α-Fe_2O_3 photoanodes was introduced. Then, the recent development of modulation strategies to promote the PEC performance of α-Fe_2O_3 was summarized.

In chapter 2, an ultrathin cobalt-manganese (Co-Mn) nanosheet, consisting of amorphous $Co(OH)_x$ layers and ultrasmall Mn_3O_4 nanocrystals, was designed as an efficient co-catalyst on α-Fe_2O_3 film for PEC water oxidation. The uniformly distributed Co-Mn nanosheets lead to a remarkable 2.6-fold enhancement on the photocurrent density at 1.23 V vs. reversible hydrogen electrode (RHE) and an impressive cathodic shift (~200 mV) of onset potential compared with bare α-Fe_2O_3 film. Furthermore, the decorated photoanode exhibited a prominent resistance against photo-corrosion with an excellent stability for over 10 h. Detailed mechanism investigation manifests that incorporation of Mn sites in the nanosheets could create electron donation to Co sites and facilitate the activation of OH group, which drastically increases the catalytic activities for water oxidation. These findings provide valuable guidance for designing high-performance co-catalysts for PEC applications and open new avenues towards controlled fabrication of mixed metallic composites.

In chapter 3, in order to reinforce the interfacial interaction at the α-Fe_2O_3/co-catalyst interface, a novel charge transfer system for PEC water oxidation was designed by inserting the MXene nanosheets (MNs) between α-Fe_2O_3 and co-catalyst. In this system, MNs acted as the hole transfer mediators to efficiently suppress the charge recombination owing to the high hole mobility of MNs and the formation of built-in electric field at the MNs/α-Fe_2O_3 junction. Meanwhile, the co-catalyst layers, in turn, could protect the MNs from oxidation to achieve prominent stability. The optimized photoanode system achieved a photocurrent density of 2.54 mA cm^{-2} (a maximum value of 3.20 mA cm^{-2} under front illumination) at 1.23 V vs. RHE. An impressive cathodic onset potential shift of ~250 mV was obtained with the synergistic effect of MNs and co-catalyst (Co-Pi). This versatile strategy could also be extended to other systems based on different semiconductors and co-catalysts, providing a promising design strategy for efficient photogenerated charge separation to enhance the PEC water oxidation.

In chapter 4, direct chemical interaction was constructed at the interface of α-Fe_2O_3 and carbon nanosheets with single-nickel sites (Ni-NC) to accelerate the reaction kinetics by providing additional charge transport channels and abundant active sites. The interfacial carrier path induced by the chemical coupling and the efficient single-nickel sites work collaboratively, achieving an impressive photocurrent density of 1.85 mA cm^{-2} at 1.23 V vs. RHE, up to 2.2 times higher than that of pure α-Fe_2O_3. These findings shed light on an interface modulation strategy and provide an alternative towards utilizing unique single active sites for efficient photoelectrochemical water splitting.

In chapter 5, an overall summary of this dissertation work was presented. This thesis carried out a systematic study on the surface/interface modulation of α-Fe_2O_3-based photoanodes for efficient PEC water oxidation. In α-Fe_2O_3-based PEC water oxidation system, co-catalysts decoration has been demonstrated to be the most efficient way to lower the reaction barrier with abundant active sites and promote charge injection to the reactants. And the delicate interface engineering between the α-Fe_2O_3 and the co-catalysts is critical for promoting charge transfer from the bulk of α-Fe_2O_3 to the co-catalysts, which can directly influence the surface catalysis. The relevant findings in this study deepen the understanding of α-Fe_2O_3-based PEC water oxidation system and highlight the importance of semiconductor/co-catalyst interface modulation for the overall photoelectrocatalytic processes.