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論　文　内　容　要　旨

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学位論文題目	Investigation of Semiconductor Photoanodes for Photoelectrocatalytic Water Splitting （光電気触媒による水分解用半導体光陽極に関する研究）		

内容要旨

Collecting and storing solar energy in hydrogrn, as plant accomplishes through photosynthesis, is a highly desirable approach to solving the questions of energy shortage and environment pollution. Photoelectrochemical water overall splitting cell is a promising system to achieve this target. It composes by ohmic contacted semiconductor photoanode and photocathode. Now the water splitting performance of photoanode is not high enough, so that influence the performance of PEC water overall splitting cell. There are two main disadvantages to limit the property of photoande. For the one, the transfer capacity of the photogenerated carriers in the photoanode is relative weakness. The other one is that the oxidation energy barrier of the photoanode is too high to limit the water oxidation reaction by photogenerated holes.

Fabrication of crystal point defect (oxygen vacancy) on the surface of the semiconductor has been proved a feasible method to resolve above disadvantages, so that can improve the PEC performance of the photoanode. However, the mechanism is still not clear. Furthermore, to date, only point defects have been employed to modify the photoanode. Other two type of crystal defects, such as line defects and planar defects, have not been studied in this area. So, In this thesis, the modification mechanism of oxygen vacancy on Mo-doped $BiVO_4$ photoanode was investigated. Then the line defect (dislocation) has been prepared on the WO_3 nanoflower photoanode, and the functions of the line defect during PEC water splitting have been investigated also.

Firstly, electrochemical reduction method has been employed to treat the surface of Mo-doped $BiVO_4$ (BiMoVO) photoanode. Further experimental data indicated that when the reduction potential located at -0.8 V (vs Ag/AgCl), quasi-oxygen vacancy formed on the (020) facet (only Bi-O bonds cracked on this facet), the electrons mobility of the BiMoVO photoanode increased dramatically, and the PEC current density of it is improved largely. However, with the reduction potential increasing to -1.2 V, oxygen vacancy formed on the surface of (020) facet (both Bi-O and V-O bonds cracked on this facet simultaneously), the PEC current density is decreased obviously. Both experimental and Density Functional Theory (DFT) calculation data pointed out that a moderate level of reduction is a key factor for the adjustment of photoanode performance. Thus, these results demonstrate firstly that oxygen vacancyactually is not the positive factor to improve the PEC performance of a $BiVO_4$ photoelectrode, but the quasi-oxygen vacancy forming on the surface of the active facet is.

Secondly, well-defined WO_3 nanoflower (NF) photoanodes were fabricated. The sharp-edage mountain like structure of the titaninum substrate play an important role to induce the WO_3 NF structure growth on it. The sharp edge of etched Ti substrate can provide an orientation force to control the nucleus growth process of WO_3 nanosheets, and finally to fabricate a flower-like WO_3 thin film after hydrothermal growth. The WO_3 NF photoanode with 8 hours growth time shows the best PEC performance, a 1.8 mA/cm^2 photocurrent density (bias potential 1 V vs Ag/AgCl) could be achieved in $NaSO_4$ electrolyte under 100 mW/cm^2 AM 1.5G simulate sun light illumination.

Lastly, point defect such as oxygen vacancy in semiconductor, has been widely evidenced that it can influence the separation and transfer processes of the photogenerated hot charges. Except point defect, to date, scarcely any study focused on expounding the functions of line defect (such as dislocation) in the crystal of semiconductor photoanode and how to influence the photogenerated hot charges separation process. Herein, edge dislocations were found distributed on the WO_3 NF crystal photoanode, inducing mismatch of (002) and (020) facets. Further photoelectrochemical performances and DOS calculation results indicated that similar with surface facet heterojunction, a heterojunction system could be formed along the dislocations line due to the energy difference between the (002) and (020) facets. So, this present study provided a new understanding of the line defect in the photogenerated hot carrier separation process, and provided a novel method to improve the properties of photoelectrodes and photocatalytic materials in the near future.