学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Construction of Hematite-based Photoelectrochemical Cells for Visible Light Water Splitting

（ヘマタイト系光電気化学セルの構築および可視光照射下における水分解に関する研究）

Photoelectrochemical (PEC) water splitting has been widely researched since 1970s as it is a promising method for solar energy conversion. Among the various semiconductors, iron-based photoelectrodes such as hematite have been extensively studied because of its visible light responsibility, earth abundant property, non-toxic and high stability. However, hematite has a very short lifetime of excited state carrier and hole diffusion length that significantly limits its efficiency in charge separation and collection as a PEC anode. And overall solar water splitting using PEC devices are still faced with great challenges due to lack of p-type photocathodes.

In order to improve the photo-to-electricity efficiency, three strategies are proposed in this work. Firstly, as the high recombination (<0.1 s) rate is one of the biggest chanllenges, forming junctions are commonly used ways to improve the charge separation efficiency in photoelectrodes via constructing a large magnitude of interfacial electric field in it. And construction of homojunction in hematite can be realized by self-doping method. Secondly, as the water oxidation rate on electrodes is relatively lower (> 1s) than the charge recombination rate, oxygen evolution catalyst can be loaded on the surface of hematite to increase the charge transfer kinetics between the electrode/electrolyte interfaces. Finally, as $LaFeO_3$ has a perovskite structure, the nearly 180º B-O-B atom chains inside the ABO_3 structure could offer an ideal three-dimensional transportation channel for photo-excited carriers, and make it a promising candidate for photoelectrochemical water reduction.

In chapter 1, general background about photoelectrochemistry and a simple overview of iron-based photoelectrodes is introduced.

In chapter 2, bilayer self-doped hematite films were fabricated for superior PEC activities and the electron/hole separation efficiency in the homojunctions were researched. Hematite layers with different Fermi Levels were successfully fabricated by controlling the oxygen vacancy densities in them and then combined into junctions. Due to the formation of homojunction inside the hematite electrodes, high charge

separation efficiency were realized via constructing a large magnitude of interfacial electric field in it. And the high oxygen vacancy layer was protected by the formation and the outer low-vacancy-layer. By designing of homojunction, photocurrent density increased to nearly 5 times with lower onset potential and higher stability.

Chapter 3 focused on nanostructured FeOOH decorated hematite and the charge transfer properties between electrode/electrolyte interfaces. After the decoration of FeOOH, the onset potential decreased 140 mV while the photocurrent density improved nearly 4 times under AM 1.5 G illumination. It is proved that the high reaction area for the nanostructured morphology and high electrocatalytic activity of FeOOH increased the amount of photogenerated holes involved in the water oxidation reaction and accelerated the kinetics of water splitting. As a result, we demonstrated that the nanostructured FeOOH has great potential for application in PEC water oxidation as cocatalysts.

In chapter 4, hematite photoanode was connected with a p-type $LaFeO_3$ photocathode into a tandem cell for overall water splitting under visible light. After systematically studied the relationship between the area of electrodes and the PEC performances of n-Fe_2O_3/p-$LaFeO_3$ tandem cells, it is proved that the activity of this photocell is mainly determined by the activity of p-$LaFeO_3$ photocathode. Finally, an all-iron-based n-Fe_2O_3/p-$LaFeO_3$ tandem cell was obtained with high activity (H_2=11.5 μmol/h; O_2=5.7 μmol/h) for more than 120 hours.

In summary (Chapter 5), this thesis carried out a systemaltic study on constructing new hematite-based photoelectrochemical cells for visible light water splitting. By controlling the oxygen vacancy densities in hematite, the Fermi level of them can be tuned and further made into homojunctions. The formation of homojunction facilitated the efficient charge separation within the electrode. While decoration of FeOOH nanosheet cocatalyst improved the charge transfer kinetics at the electrode/electrolyte interface. The designing of Fe_2O_3/$LaFeO_3$ tandem cell demonstrated that the p-type photocathodes limited the whole performance of the photocell. This study opened up a perspective strategy towards obtaining efficient, highly-stable and low cost hematite-based PEC water splitting systems in the future research.