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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 リ シジェ

学位論文題名

## Surface/Interface Engineering of Si-based Photocathodes for Efficient Photoelectrochemical Hydrogen Production (表面/界面制御によるシリコン系光電極の効率的な光電気化学水素生成に関する研究)

Photoelectrochemical (PEC) water splitting is a promising approach to directly convert solar energy into hydrogen fuel. As an attractive light absorber, p-type crystal Si has been intensively studied as a photocathode to carry out PEC hydrogen evolution reaction (HER) due to its earth abundance and remarkable light-harvesting ability (1.12 eV bandgap). However, the easy corrosion of Si in electrolyte solution leads to poor stability, and the excited electron-hole pairs inevitably recombine at the Si/electrolyte interface, causing sluggish surface kinetic for HER. In this regard, the design of Si-based photocathodes with sufficient surface catalytic activity and facile interfacial charge transport should be considered to improve the efficiency and stability of solar-to-hydrogen conversion, especially when low-cost cocatalysts have been developed over the past decades. Therefore, this thesis focused on rational Si surface modification for sensitive photocurrent response, cocatalyst design for high photovoltage, and interface engineering by inserting functional protection layer between Si and cocatalyst for robust stability and rapid charge-transfer kinetics.

In chapter 1, a general background about photoelectrochemistry and a brief overview of Si-based PEC HER were introduced. Then, the recent development of surface/interface engineering strategies (including etching Si photonic textures, loading cocatalysts, introducing protection layers, and fabricating junction structures) to promote the PEC performance of Si photocathodes was summarized.

In chapter 2, an amorphous Si (a-Si) layer was in-situ co-deposited with Pt nanoparticles onto crystal Si (c-Si) photocathode through electroless method, forming a structure of Pt/a-Si/c-Si, in order to facilitate electron transfer from c-Si to Pt. Compared with the Pt/c-Si photocathode, the a-Si layer within Pt/a-Si/c-Si can not only act as an electron transfer mediator but also as a good passivation layer, producing a high-quality a-Si/c-Si buried junction for enhanced photovoltage and photocurrent response. The resulting a-Si/c-Si interface has a large energy band shift simultaneously, forming a potential barrier to suppress carrier recombination and ensure charge transfer. In addition, the a-Si layer serves as the growth substrate of the cocatalyst, which could effectively modulate the size and distribution of Pt nanoparticles to be smaller and more uniform. This Pt/a-Si/c-Si photocathode presented an onset potential of +0.42 V vs. reversible hydrogen electrode (V<sub>RHE</sub>) and a photocurrent density of 35.0 mA cm<sup>-2</sup> at 0 V<sub>RHE</sub> in 0.5 M H<sub>2</sub>SO<sub>4</sub>. This study provides a feasible manner to improve the photoresponse of Si-based photocathodes based on the construction of surface Si junction structures.

In chapter 3, a NiS<sub>2</sub>/NiS heterojunction (NNH) was designed and applied to a planar p-type Si (p-Si) substrate as an effective cocatalyst to achieve progressive electron transfer. The NNH/Si photocathode exhibited an onset potential of  $+0.28 \text{ V}_{\text{RHE}}$  and a photocurrent density of 18.9 mA cm<sup>-2</sup> at 0 V<sub>RHE</sub>, as well as a 0.9% half-cell solar-to-hydrogen efficiency, which is much superior compared with those of NiS<sub>2</sub>/Si and NiS/Si photocathodes. The enhanced performance for NNH/Si was attributed to the contact between the n-type semiconducting NNH and the planar p-Si semiconductor through a p-Si/n-NiS/n-NiS<sub>2</sub> manner that functions as a local pn-junction to promote electron transfer. Thus, the photogenerated electron was transferred from p-Si to n-NiS within NNH as the progressive medium, followed by Ni<sup>2+</sup> and/or S<sub>2</sub><sup>2-</sup> of the defect-rich n-NiS<sub>2</sub> phase as the key active sites. This research may pave the way for planar Si-based PEC applications of heterogeneous metal sulfide cocatalysts through the progressive transfer of electrons.

In chapter 4, to reinforce the interfacial interaction at the Si/cocatalyst interface, a synergetic coupling of the anti-reflective Co-P cocatalyst and the anti-corrosive WS<sub>x</sub> interlayer on planar p-Si photocathode was investigated for efficient and durable PEC HER in alkaline media. The thin-film WS<sub>x</sub> interlayer plays a trifunctional role in 1) protecting Si substrate from alkaline corrosion, 2) providing an appropriate nucleation base for the morphology optimization of Co-P cocatalyst, and 3) promoting the electron transfer from photocathode to the electrolyte. The Co-P cocatalyst could be modulated by controlling thin-film WS<sub>x</sub> morphology to have the least light-blocking effect but retain the catalytic activity. The complementary integration of the Co-P film cocatalyst on WS<sub>x</sub>/Si photocathode exhibited superior catalytic properties (onset potential of +0.47 V<sub>RHE</sub>, photocurrent density of -25.1 mA cm<sup>-2</sup> at 0 V<sub>RHE</sub>), which benefits from the significantly enhanced reaction kinetics by promoting electron transfer. Meanwhile, through such a rational structure, the optimal Co-P/WS<sub>x</sub>/Si photocathode showed long-term stability of 300 h at a high photocurrent density above -25 mA cm<sup>-2</sup> at 0 V<sub>RHE</sub> without noticeable degradation. These findings offer a facile and effective interface modulation approach for the further development of durable Si-based photoelectrochemical devices.

In chapter 5, an overall summary of this dissertation work was presented. This thesis carried out a systematic study on the surface/interface engineering of Si-based photocathodes for efficient and durable PEC hydrogen evolution. In the Si-based PEC-HER system, the inert active surface and easy corrosion of Si can be effectively alleviated through surface-supported cocatalysts. More importantly, the selection and optimization of cocatalysts, as well as suitable surface/interface engineering between Si and cocatalysts are also the keys to further offer tunable optical properties, high mechanical stability, and rapid charge transfer. This thesis progressively revealed that Si surface modification, cocatalyst optimization, and introduction of functional interfacial layer between Si and cocatalyst were of great significance for improving the PEC-HER performance. The relevant findings in this study deepened the understanding of Si-based PEC-HER application, and provided a potential surface/interface engineering strategy for constructing Si-based photocathodes with a high-quality interface and enabling efficient hydrogen production.