別紙４－１（課程博士（英文））

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# Abstract（Doctor）

| Title of Thesis | Development of efficient photoelectrodes for photoelectrochemical water splitting and hydrogen generation |
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Approx. 800 words


Photoelectrochemical water splitting (PEC-WS) technique that uses solar energy and photoelectrodes immersed in an electrolyte has sparked an increased interest to generate chemical energy, such as $H_2$ in one step. The important requirements to achieve an efficient PEC-WS system are (1) absorbing a wide wavelength range of solar energy; (2) excellent $e^-/h^+$ pairs separation and mobility; (3) low overpotential for $H_2$ and $O_2$ evolution reaction; (4) high stability; (5) scalable techniques and (6) low-cost materials. The main objective of this thesis is to present simple methods for designing efficient and stable photoanodes for PEC-WS that generate large amount of $H_2$. Our approach focuses on improving the optical and electrical properties of some metal oxides by the deposition of appropriate quantity of metal chalcogenides (MCs) and plasmonic metal nanoparticles (NPs). The distinctive electrical and optical characteristics of MCs have made them promising choice for light absorbers. The decoration of metal oxide semiconductors with plasmonic metal NPs has also been reported as an auspicious approach for promoting the PEC performance by the transfer of plasmonic energy from the plasmonic metal NPs to the metal oxide semiconductor.

This thesis consists of four studies for designing and investigating photoanodes for PEC-WS; (1) Anodized nanoporous (ANPor) $WO_3$ was decorated with $Bi_2S_3$ quantum dots (QDs) and investigated as a photoanode for PEC-WS under ultraviolet-visible (UV-Vis) illumination. The ANPor $WO_3$ photoanode decorated with ten cycles of $Bi_2S_3$ QDs exhibited the highest current density of 16.28 mA $cm^{-2}$ at 0.95 V vs. reversible hydrogen electrode (RHE), which is ~ 19 times than pure ANPor $WO_3$ (0.85 mA $cm^{-2}$). Furthermore, ANPor $WO_3/Bi_2S_3$ QDs (10) photoanode demonstrated the highest ABPE of 4.1% at 0.66 V vs. RHE, while pure ANPor $WO_3$ displayed 0.3% at 0.85 V vs. RHE. This was ascribed to the proper deposited quantity of $Bi_2S_3$ QDs which remarkably enhanced the Vis light absorption, and the formation of type-II band alignment between $WO_3$ and $Bi_2S_3$ QDs which improved $e^-/h^+$ pairs separation and migration.

(2) The unique morphology of ZnO nanopagoda arrays (NPGs) was prepared using aqueous downward growth technique, followed by deposition of various quantities of Ag NPs.

The deposition of an optimal quantity of Ag NPs over ZnO NPGs demonstrated the highest photocurrent of 2.15 mA $cm^{-2}$ at 1.23 V vs RHE, meanwhile pure ZnO NRs and NPGs attained 0.90 and 1.43 mA $cm^{-2}$, respectively. This remarkable increase in photocurrent density was extensively analyzed using various PEC and optical determinations as well as electromagnetic simulation. As a result, this improved PEC performance was ascribed to two reasons; firstly, ZnO NPGs can mitigate the charge recombination rate owing to the reduced structural defects and enhance the light absorption ability owing to their distinct superstructure properties. Secondly, the deposition of plasmonic Ag NPs can improve the interfacial charge transfer and raise the ability to absorp Vis light due to their LSPR effect.

(3) ZnO NPGs was modified with Ag and $Ag_2S$ NPs and investigated as a photoanode for the PEC system. The crystal structure, morphology, elemental composition, optical characteristics, and PEC performance of the prepared samples were studied. The results revealed that, the successful deposition of Ag and $Ag_2S$ NPs on the surface of ZnO NPGs not only improved the Vis light absorption but also ameliorated the $e^-/h^+$ pairs separation and transfer. The optimum amount of Ag-$Ag_2S$ NPs on ZnO NPGs attained the maximum photocurrent of 2.91 mA $cm^{-2}$ at 1.23 V vs. RHE, about five times than pure ZnO NPGs. It also exhibited the improved ABPE of 0.43% at 0.6 V vs. RHE. This study presented a facile preparation process of a unique ZnO NPGs and enhanced PEC performance through the synergistic effect of the LSPR of Ag NPs and Vis light sensitization of $Ag_2S$ NPs.

(4) An effective type II heterojunction between $Bi_2Se_3$ QDs and $TiO_2$ nanotube arrays (TNTAs) was formed by depositing $Bi_2Se_3$ QDs on the surface of TNTAs. The TNTAs/$Bi_2Se_3$ QDs photoanode displayed the highest photocurrent density of 1.75 mA $cm^{-2}$, which is 3.8 times higher than pure TNTAs (0.46 mA $cm^{-2}$) at 1.23 V vs. RHE. They also achieved a high $H_2$ generation amount of 355.8 μmol after 5 hours, which is 3.3 times higher than pure TNTAs (105.3 μmol) at 1.23 V vs. RHE. TNTAs and TNTAs/$Bi_2Se_3$ QDs photoanodes both demonstrated superb stability for over 7 hours. The TNTAs/$Bi_2Se_3$ QDs photoanode demonstrated higher IPCE in the UV region than pure TNTAs and extended the light response to the Vis region owing to its lower charge recombination rate and the Vis light absorption ability derived from $Bi_2Se_3$ QDs. The superb PEC performance of TNTAs/$Bi_2Se_3$ QDs photoanode was also owing to its suitable bandgap energy, which improved the Vis light absorption, and its efficient charge transfer, that alleviated the $e^-/h^+$ pairs recombination. Consequently, this thesis paves the way for facile approaches to construct efficient photoanodes for PEC-WS and $H_2$ generation.