

Abstract

The ever-growing demand for clean and sustainable energies urges us to expand the use of renewable energies and to develop new energy conversion routes. One of viable options is light-driven water splitting into hydrogen that is promising strategy to store solar energy in the form of chemical bonds. Since there is no carbon dioxide as a by-product released in the process, this research area is favored as a practical way of accomplishing the green energy production. In essence, water splitting is a redox reaction that could be comprehended in terms of two redox half-reactions; the cathodic half-reaction refers to the reduction of two aqueous protons to one molecule of hydrogen, and the anodic half-reaction corresponds to the oxidation of two H₂O molecules to one O₂ molecule. Importantly, these two half-reactions could be independently investigated at their mechanisms and then be recombined together to examine the overall hydrogen productiveness. Among many pathways proposing for the conversion of water into hydrogen induced by sunlight, the photoelectrochemical and photocatalytic water splitting based on TiO₂ semiconductor have attracted more attention of scientists because of the low toxicity, abundance and high stability under the water splitting reactions. While TiO₂-based hydrogen production work under ultraviolet irradiation, due to the large band gap ($E_g = \sim 3.2$ eV) of TiO₂, the dye-sensitization of TiO₂ which is a simple and effective approach to extend the absorption range of wide energy gap semiconductors has been attempted.

While metal-containing dyes were decent sensitizers and showed high catalytic activities, they are typically suffered from the low molar extinction coefficients ($\epsilon < \sim 20000$ M⁻¹ cm⁻¹). In contrast to the weak absorption of inorganic dyes, the molar extinction coefficients of some organic dyes are an order of magnitude higher ($\epsilon > \sim 10^5$ M⁻¹ cm⁻¹). Additionally, due to their profitable properties such as inexpensive, wide structural variety and tenability, the use of metal-free organic dyes as photosensitizers have been investigated. To utilize solar energy efficiently, an ideal sensitizer is required to absorb sunlight thoroughly in a broad wavelength region, so that more photons could be captured to drive the water splitting reactions. However, metal-free organic photosensitizers mainly reported to date only cover a narrow range in the visible-light region. Indeed, given by the fact that sunlight spectrum not only consists of UV and visible region but also nearly 48% consists of near-infrared and infrared radiation, synthesis of metal-free organic photosensitizers that are capable to harvest wide light region are worth to be studied. The lack of reports on the use of near-infrared dyes for the application in TiO₂-based hydrogen production research has prompted us to explore 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) as the dye of choice, which possesses a high molar extinction coefficient and excellent photostability. Taking advantage of their

photochemical and photophysical properties that tunable upon molecular engineering, π -extended BODIPY dyes were proposed, which absorbed near-infrared light strongly. In this research, we focus on the use of visible to near-infrared absorbing dibenzo-BODIPY in application of dye-sensitized photoelectrochemical (DSPEC) and dye-sensitized photocatalytic (DSP) water splitting for hydrogen production.

This thesis was organized into 4 chapters. Chapter 1 has given an introduction to the urgent need of creating new energy materials and the principle of DSPEC and DSP systems, as well as the motivation for dye-sensitized hydrogen production using near-infrared absorbing dye. Furthermore, the properties of dibenzo-BODIPY is discussed.

In chapter 2, I describe DSPEC cell with near-infrared absorption capability to accomplish the full water splitting. The design of a new strongly absorbing dibenzo-BODIPY dye that contains rhodanine moiety as an anchoring group is presented. The targeted dye was synthesized and its properties in THF showed λ_{\max} 687 nm with high molar extinction coefficient ($\epsilon = 1.09 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$). Although the absorption maximum was peaked in the visible region, the onset of the near-infrared absorption at the λ_{onset} of 728 nm was observed. For electrochemistry and photoelectrochemistry measurements, the photoanodes were fabricated through the co-deposition of synthesized dye with water oxidation catalyst onto FTO/TiO₂ electrode. The resultant photoanode operated as working electrode in photoelectrochemical water oxidation. Photocurrent were generated under irradiation ($\lambda > 400 \text{ nm}$) using Xe lamp 300 W with 100 mW cm^{-2} light intensity. Following 2000 seconds photolysis for the photoanode, hydrogen (H₂) and oxygen (O₂) were detected by gas chromatography with Faradaic efficiencies reaching 65.8% and 76.4% for H₂ and O₂, respectively.

Chapter 3 presents the utilizing solar energy for the hydrogen generation from aqueous proton to drive the reductive half-reaction of water splitting through dye-sensitized photocatalyst (DSP). A dibenzo-BODIPY-incorporated phenothiazine dye was synthesized, which exhibited an intense absorption band at 638 nm with high molar absorptivity ($\epsilon = 1.23 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) and an additional peak at 440 nm ($\epsilon = 1.80 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) in THF solution. The dye immobilized onto platinized-hierarchical porous TiO₂ (Pt/HPT500) photocatalyst served as a panchromatic photosensitizer with a broad absorption up to 780 nm. The resultant photocatalysis was investigated in the presence of ascorbic acid as a sacrificial electron donor in phosphate buffer solutions to show excellent hydrogen production with high turnover number (TON) when irradiated with $\lambda > 400 \text{ nm}$ using Xe lamp at 100 mW cm^{-2} light intensity.

Lastly, in Chapter 4 the principal findings and results are summarized, and a suggestion for future work is presented.