可視-近赤外光応答可能な有機色素の開発と光触媒水分解に関する研究

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https://hdl.handle.net/2324/7182545

出版情報：Kyushu University, 2023, 博士（工学）, 課程博士
バージョン：

（様式３）

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区　　分　：甲

論文内容の要旨

The study focused on modifying organic dyes for enhanced responsiveness to visible and near-infrared light. In addition, one of the key aspects was to explore the charge transfer mechanism in the photocatalytic reaction. Series of organic dyes have been synthesized and systematically investigated for their reaction mechanisms, including one dye with a squaraine based structure and six dyes with a boron-dipyrrolylidinediamine (BODIPY) based structure. These studies not only broaden our understanding of the application of these organic dyes, but also contribute to our continual search for superior photocatalytic materials, which has deep implications for the renewable energy field.

In the chapter 1, the research background covered from the hydrogen production methods to recent advancements in visible to near-infrared light-sensitive materials. The purpose of the study was also discussed in detail.

In chapter 2, squaraine dye was synthesized as a dye sensitizer for a dye-sensitized photocatalytic system, which was composed of pyridyl-anchored squaraine dye and Pt-loaded TiO_2 powder photocatalyst. The squaraine dye/platinum (Pt)-TiO_2 system exhibited a good hydrogen production performance within 150 h and an apparent quantum yield (AQY) of 1.4% under 800 nm monochromatic light irradiation. However, during the photocatalytic reaction, the photocatalytic activity of squaraine dye/Pt-TiO_2 decreased due to photodecomposition. Ultraviolet–visible absorption spectroscopy, ^1H nuclear magnetic resonance spectroscopy, and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry measurements were performed to investigate the mechanism of the decomposition of the squaraine moiety of squaraine, the decomposition process, and the structure of the decomposed material. The results show that even without the Pt-loaded TiO_2 powder photocatalyst, squaraine dye undergoes photodissociation, which cleaves the bond between the indoline moiety and the squaraine.

In chapter 3, BODIPY compounds were extensively utilized in various applications. Typically, their activity was modified by altering the functional groups at the *α*−, *β*−, and *meso*− positions of the substituents. However, no systematic information was provided on the effect of substituted F−positions and hydrophobicity on the activity of BODIPY sensitizers in photosensitizing chemistry. Dyes with different alkyl chain lengths were synthesized and compared with parent BODIPY structure to discuss the effect of −F position substituents and hydrophobicity of BODIPY dyes on photocatalytic activity. Density functional theory (DFT) calculations showed that −F substitution induced an intramolecular charge transfer (ICT) effect, enhancing visible light absorption. Longer alkyl chains provided a favorable second coordination sphere reaction environment for hydrogen production. Experimentally, dye with dodecyloxy group demonstrated the highest activity, with a hydrogen production rate of 496.5 $\mu mol \cdot gcat^{-1} \cdot h^{-1}$ which was 3 times higher than

parent BODIPY structure, and 9.6 times higher turnover frequency (TOF) than parent BODIPY structure. An AQY at 650 nm showed 1.4%. This study highlighted the importance of −F position substitution and optimizing hydrophobicity to enhance the photocatalytic activity of metal-free organic dyes through the creation of a new second coordination sphere.

In chapter 4, donor-π-acceptor (D-π-A) type dye-sensitizer had recently attracted considerable attention, due to the properties of dye sensitizers could be changed by adjusting each unit. A 3 kinds of D-π-A type dye sensitizers which consist of different amounts of thiophene as π-spacers were designed and synthesized and tested photocatalytic activity under visible light (>420 nm) irradiation. Carbazole-terthiophene containing terthiophenes had the highest catalytic activity with a catalytic turnover frequency (TOF) of 1505 h^{-1}. And the AQY of carbazole-terthiophene containing dye/Pt-TiO_2 (micro-flower) under 950 nm monochromatic light irradiation was 0.2%, which was the highest efficiency among the reported hydrogen production performance of dye-sensitized system. Photocurrent, optical impedance, time-resolved absorption measurements were used to discuss the effects of π-spacers. As the number of thiophene increases, the electron recombination rate became slower, thus allowing more excited electrons could be injected into TiO_2 to participate in the photocatalytic reaction.

In chapter 5, summarizes each section of this thesis and provides an outlook on potential contributions to future research areas.