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学位論文題目 Design and Construction of Framework Catalysts for  
Hydrogen Evolution

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Summary (Abstract) of doctoral thesis contents

The photocatalytic reduction of water molecule into dihydrogen ( $H_2$ ) is known as a promising way to provide a sustainable and environmentally friendly chemical energy. Therefore, several efforts have been made on the construction homogeneous systems using various combinations of molecular-based catalysts and photosensitizers. A great advantage of such homogenous systems is that we can understand their reaction mechanisms in detail based on well-established spectroscopic techniques. The nature of the systems allows us to precisely tune their structures/properties, which results in improved catalytic activities. However, these system are considered to have difficulty for practical application due to their moderate stability and low reusability, for which heterogeneous photocatalytic systems are rather advantageous. Based on the background, in this study, we aimed to develop novel molecular-based catalytic system, in which the advantages feature of homogeneous and heterogeneous system are integrated.

In this doctoral thesis, after the General Introduction, the development of a novel heterogeneous photocatalytic system for  $H_2$  evolution is reported in Chapter 1. I propose that a heterogeneous photocatalytic system can be constructed by the supramolecular assembly of discrete molecules. In this system, a discrete catalyst module (**CM**), which contains metal complex-based catalytic centre (catalytic node) and intermolecular connection sites (molecular connector), can be assembled into an ordered structure through non-covalent interaction to afford a heterogeneous framework catalyst (**FC**). Unlike assembly driven by coordination bonding, known as coordination polymers, catalyst modules can easily be assembled/disassembled simply by changing solvents while maintaining the structure of the active sites. Therefore, my system can reveal two prominent features; (1) well-defined catalytic sites attributed to the molecular-based modules and (2) reusability and high durability based on the heterogeneous nature.

Based on the aforementioned strategy, I employed a Rh(II) dimer complex bearing 1,8-naphthalimide-based ligands,  $Rh_2(NIP)_4$  (**CM-1**, **HNIP** = 3-(1,8-naphthalimido)-propanoic acid) as a catalyst module. The Rh(II) paddle-wheel moiety is expected to serve as catalytic center and is suitable for the construction of ordered structures due to its high ( $D_{4h}$ ) symmetric structure. 1,8-Naphthalimide unit can serve both as a light-harvesting unit for the photocatalytic reaction and a functional moieties to construct intermolecular interactions. **CM-1** was successfully synthesized by the ligand exchange reaction between **HNIP** and  $Na_4[Rh_2(CO_3)_4] \cdot 3H_2O$ , and characterized by several spectroscopic analysis techniques and elemental analysis. Subsequently, the self-assembly of **CM-1** to construct a framework catalyst (**FC-1**) was performed by the slow diffusion of  $CHCl_3$  into a DMSO solution of **CM-1**. The single-crystal X-ray structure analysis of the obtained crystal reveals the formation of framework structure stabilized by the intermolecular via  $\pi$ - $\pi$  stacking interactions between the aromatic rings of the **NIP** ligands. The result clearly indicates that the framework catalyst (**FC-1**) can be constructed via the self-assembly of **CM-1**.

I also investigated the photophysical properties of **CM-1** and **FC-1**, and it was found that the excellent light-harvesting property of 1,8-naphthalimide units are retained. Subsequently, electrocatalytic activity of **CM-1** and **FC-1** was examined by cyclic voltammetry. Cyclic voltammograms of **CM-1** and **FC-1** exhibited a large irreversible current attributed to the electrocatalytic  $H_2$  evolution in the presence of acetic acid. Note that catalytic

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reaction did not proceed in the absence of acetic acid, indicating that the interaction between acetic acid and the Rh<sub>2</sub> centre generates the catalytically active Rh<sub>2</sub>-H species to promote catalytic hydrogen evolution both in solution and the solid state.

The photocatalytic activity of **FC-1** was consequently examined in an aqueous acetate buffer solution (pH = 5) containing EDTA-2Na (0.2 M) as a sacrificial electron donor. Upon light irradiation ( $\lambda > 320$  nm), the production of H<sub>2</sub> linearly increased with time. The initial reaction rate (TOF) for 1 h was determined to be 67  $\mu\text{molg}^{-1}\text{h}^{-1}$  and the turnover number (TON) reached to 3.5 after 75 h. Several control experiments demonstrated that integration of the photosensitizer (1,8-naphthalimide moiety) and the catalytic centre (Rh<sub>2</sub><sup>III</sup> paddle-wheel unit) into the same molecule is crucial for photocatalytic H<sub>2</sub> production. I also investigated the stability and the reusability, and it was found that the catalytic activity of **FC-1** was maintained after 70 h of photoreaction, and the catalyst can be reused at least for three cycles without considerable loss of the activity. I also found that the intramolecular oxidative quenching of **NIP\*** by the Rh<sub>2</sub> centre was a key step to generate the catalytically active Rh<sub>2</sub>-H species.

Chapter 2 describes the development of photo-active catalyst with visible-light absorbing dye moieties. I chose boron dipyrromethene dye (BODIPY; **BDP**), as a visible-light absorbing unit because the chromophore is known to exhibit intense absorption bands in yellow-green region and rich electrochemical properties. The new Rh(II) dimer complex bearing bodipy-based ligands, Rh<sub>2</sub>(**BDP**)<sub>4</sub> (**CM-2**, **HBDP** = 1,3,5,7-tetramethyl-8-(4-carboxyphenolic)-BODIPY acid) was successfully synthesized and characterized. I also succeeded in constructing a framework catalyst (**FC-2**) by the self-assembly of **CM-2** and the structure of **FC-2** was determined by the single-crystal structural analysis. Cyclic voltammetry and controlled-potential electrolysis of **CM-2** and **FC-2** confirmed the electrocatalytic activity of **CM-2** and **FC-2** for H<sub>2</sub> production. I subsequently investigated the photocatalytic activity of **CM-2** for hydrogen evolution under visible light irradiation. Irradiation of visible light ( $\lambda_{\text{irr}} > 370$  nm) to a solution of **CM-2** (0.1 mM) in THF/water containing BIH (1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzimidazole) as a sacrificial electron donor results in the generation of dihydrogen as confirmed by gas chromatography. Several control experiments were also conducted to further clarify the catalytic activity of **CM-2** in detail.

In Chapter 3, investigation of a framework catalyst by high energy X-ray measurements (HEXS) and pair distribution analysis (PDF) is reported. X-ray scattering results coupled with PDF analysis can reveal distances between neighbouring atoms of overall real space in solid-state. Therefore, a comparison of experimentally obtained scattering patterns with patterns calculated from coordinate model can provide the quantitative bond distances in the materials. In this study, I tried the analysis of **FC-1** by solid-state phase X-ray scattering technique and PDF analysis. By analysing the patterns, several distances in **NIP** light-harvesting moiety and the rhodium dimer catalytic centre were successfully determined. I also found the several spectral features reflecting the packing structure of **FC-1**. This outcome study demonstrates the opportunity to resolve the full inner and outer shell ligand structure for coordination complexes in solid-state.

Finally, I concluded that the novel approach to construct the catalytic system for hydrogen production was successfully developed by the self-assembly of catalyst modules via intermolecular non-covalent interactions.

太陽光のエネルギーを用いて、地球上に豊富に存在する水から有用な化学エネルギー源である水素を得ることができる光水素発生触媒系の開発は極めて意義深い。このような観点から、人工的にデザインされた材料を用いて水素発生触媒を開発する試みが数多く報告されてきた。これまでに報告されている水素発生触媒は主に金属錯体等を用いた分子性の均一系触媒、無機半導体物質を用いた不均一系触媒の2つに大別される。均一系触媒は、各種分光法を駆使した分子レベルでの反応機構解明が可能であり、また活性点の反応性を分子構造によって精密に制御できるという利点を有している。一方、不均一系触媒は、安定性・再利用性が高い点で実用化の観点から有用な材料である。そこで、本学位論文では、これら均一系・不均一系の利点を併せ持つ新規水素発生触媒材料の開発研究を目的とし、非共有結合性相互作用を用いた新たな触媒材料の開発ならびに得られた触媒の物性・反応性について報告している。以下にその概要を示す。

第1章では、非共有結合性相互作用を用いた触媒材料の開発についてまとめている。触媒部位と非共有結合性相互作用サイトを併せ持つ分子性触媒モジュールを分子間相互作用により自己集合させ、フレームワーク触媒の構築を行った。触媒部位としては、水素発生能を示すことで知られるRh(II)パドルホイール錯体を、相互作用サイトとしては、広い $\pi$ 共役系を有し、光捕集能を有する1,8-naphthalimideを選択した。分子性触媒モジュールを新規に合成した後、室温で自己集合させたところ、内部に細孔を有するフレームワーク構造が構築できることが見出された。またその構造の構築には配位子間での共有結合性相互作用が支配的に働いていることも確認している。更に、得られたフレームワーク触媒について光水素発生触媒能の評価を行っている。犠牲還元剤の存在下、フレームワークに対し紫外光を照射することで、水素発生反応が進行することを見出した。また、種々の対照実験を網羅的に実施し、フレームワーク触媒が、不均一系光水素発生触媒として機能することを実証している。加えて、このフレームワーク触媒の安定性及び再利用性についても評価を行い、その高い耐久性・再利用性についても明らかにしている。

第2章では、第1章で得られた知見を礎に、可視光吸収が可能なあらたな分子性触媒モジュールならびにフレームワーク触媒の開発に関してまとめている。可視光領域に強い光吸収を示すboron dipyrromethene (BODIPY)を配位子として有するRh(II)パドルホイール錯体を新たな分子性触媒モジュールとして設計・合成している。そして、この分子性触媒モジュールについても、自己集合によりフレームワーク構造を構築可能であることを単結晶X線構造解析により明らかにしている。この分子性触媒モジュールならびにフレームワークは電気化学的条件下で水素発生触媒として機能することを見出している。更に、分子性触媒モジュールを触媒として用いた、可視光を利用した光水素発生反応の開発についても報告している。

第3章では、第1章で開発したフレームワーク触媒の高エネルギーX線を用いたX線散乱測定ならびに対相関関数分析を実施し、その構造解析について報告を行っている。

以上のように、本学位論文では、分子性触媒モジュールの自己集合を利用した新たなフレームワークの開発ならびに得られたフレームワークを触媒として用いた水素発生反応の

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開発に成功している。また得られたフレームワークの物性ならびに反応性についても詳細に調査されており、学術的意義は大きいと認められる。以上より、博士(理学)の学位を与えるのにふさわしい学位論文であると審査員全員一致で判断した。