

## 【学位論文審査の要旨】

Solar water splitting to produce hydrogen represents one of the most promising renewable energy source to eventually achieve a sustainable environment. Since the initiation of the photo-induced water splitting by Honda and Fujishima (*Nature*, 1972, 238, 37) using  $\text{TiO}_2$ , many researchers have developed new and improved dye-sensitized photoelectrochemical cells (DSPECs), mimicking the natural process of photosynthesis (*Chem. Rev.*, 2015, 115, 13012). This project aims at developing new and robust DSPECs through the combination of ruthenium polypyridyl complexes as photosensitizers with appropriate metal oxide semiconductors such as  $\text{TiO}_2$ , ITO and  $\text{BiVO}_4$ . Such the hybrid approach targets device robustness by synthesizing new hydrophobic photosensitizers, which harvest light more efficiently and can survive under constant light irradiation. The project also targets the coupling of  $\text{BiVO}_4$  semiconductor with  $\text{TiO}_2$  or ITO nanoparticle to construct more efficient photoanodes upon interaction with metal complexes.

**Chapter 1 (Introduction)** provides the literature review of current progress in artificial photosynthesis, a variety of metal-oxide semiconductors for water splitting, recent development of ruthenium complexes for use as photosensitizers and catalysts and the review of the different types of dye-sensitized photoelectrochemical cells (DSPECs) for hydrogen production using light energy.

**Chapter 2** and **Chapter 3** discuss about the DSPECs incorporating a family of ruthenium complexes  $[\text{Ru}^{\text{II}}(\text{bipyP})(\text{bipy})_2]$  (**P1**),  $[\text{Ru}^{\text{II}}(\text{bipyP})(\text{dmb})_2]$  (**P2**),  $[\text{Ru}^{\text{II}}(\text{bipyP})(\text{dtbb})_2]$  (**P3**) and  $[\text{Ru}^{\text{II}}(\text{bipyP})(\text{dnb})_2]$  (**P4**) where bipyP = 2,2'-bipyridine-4,4'-diphosphonic acid; bipy = 2,2'-bipyridine; dmb = 4,4'-dimethyl-2,2'-bipyridine; dnb = 4,4'-dinonyl-2,2'-bipyridine that were fabricated in a dye-only system (*do*-DSPEC) and in a system where the electrolyte solution was loaded with EDTA sacrificial agent (*sa*-DSPEC) (*Chem. Commun.*, 2017, 53, 3042). In **Chapter 2**, the discussion is focused on the performance comparison between DSPEC with **P1** and that with **P4**. desorption study in pH 5.9 and pH 8.1 solutions showed that FTO/ $\text{TiO}_2$ /**P4** photoanode is better retained on the titania surface in comparison with FTO/ $\text{TiO}_2$ /**P1**. When measured using  $\text{Na}_2\text{SO}_4$  0.1 M electrolyte (pH 5.9), the immobilized **P4** in FTO/ $\text{TiO}_2$ /**P4** electrode displays higher  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  oxidation potential (1.47 V vs. NHE) than that of the **P1** counterpart (1.33 V vs. NHE). The DSPEC assembled with FTO/ $\text{TiO}_2$ /**P4** electrode shows greater photocurrent densities, higher amount of hydrogen gas, better Faradaic efficiency and greater photostability during the photolysis experiments at 0.2 V NHE (This work has been published in *Inorg. Chim. Acta.* 2018, 471, 467)

**Chapter 3** is concerned with the detailed evaluation of the energetics of the photosensitizers on  $\text{TiO}_2$  surface in relation to the variation in the alkyl chain, which influence the DSPEC performance. The increasing number of the alkyl chain of the ancillary bipy ligand shift the ground- and excited-state potentials to the more negative values although the introduction of the longer nonyl chain in **P4** shows the opposite effect. In *do*-DSPECs, the photocurrent and hydrogen production performance follows the order **P4**>**P3**>**P2**>**P1**, which correlate well with the excited state lifetimes of the dyes in solution and in  $\text{TiO}_2$  film.

The photoelectrochemistry of the *sa*-DSPECs reveals 10 times as much photocurrents as those measured in *do*-DSPECs suggesting the ability of the photo-oxidized dye (hole) to oxidize EDTA molecule. The hydrogen production performance of the *sa*-DSPECs over three hours follows the order **P2**>**P1**>**P3**>**P4**, which was consistent with the energy required for the dyes to self-exchange from  $\text{Ru}^{\text{III}}$  to  $\text{Ru}^{\text{II}}$  on titania surface. As measured by temperature-dependent cyclic voltammetry, such the reorganization energies for **P1**, **P2**, **P3** and **P4** were found to be  $2753 \pm 95$ ,  $2062 \pm 62$ ,  $2507 \pm 114$  and  $3421 \pm$

80, respectively, which gives evidence that **P2** dye has the lowest energetic cost required for the Ru<sup>III</sup>/Ru<sup>II</sup> self-exchange process, in contrast to the high value for **P4**. This study provides evidence that the subtle alkyl chain variation of the ruthenium photosensitizers can fine tune the electron injection capacity, Ru<sup>III</sup>/Ru<sup>II</sup> self-exchange energetics and photostability of the complexes, which greatly influence the performance of the DSPECs (manuscript submitted to *Dalton Transactions*)

**In Chapter 4**, the photo-electrochemical performance of BiVO<sub>4</sub>/TiO<sub>2</sub> heterojunction photoanode in combination with CuTCPP water oxidation co-catalyst (BiVO<sub>4</sub>/TiO<sub>2</sub>/CuTCPP) was evaluated. The presence of the TiO<sub>2</sub>-absorbed CuTCPP increases the photocurrent, oxygen and hydrogen quantities significantly, thus confirming the hole transfer from BiVO<sub>4</sub> to TiO<sub>2</sub> valence bands before the hole is used to activate the CuTCPP co-catalyst.

The thesis has contributed significantly to the photo-induced water splitting research through clarifying the hole transfer mechanism in both ruthenium dyes and in the heterojunction system. The result presented in this thesis will also accelerate the development of the practical water splitting devices worthy of commercialization that will lead to the contribution to the wider society. Considering the excellence and high quality research presented in this thesis, the candidate deserves the doctoral award.