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MASTER'S THESIS

Metal-organic and organic photosensitizers for photocatalytic hydrogen generation and carbon dioxide reduction

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Abstract

This thesis is focused on developing metal-organic and organic molecules for photocatalytic water splitting and carbon dioxide reduction.

In chapter 1, an overview of hydrogen production, dye-sensitized solar cells and carbon dioxide reduction are provided. The development history and reaction mechanisms of catalytic systems are introduced along with the typical examples in each field. The applications of both metal-organic and organic compounds are covered.

In chapter 2, nine molecular organic photosensitizers were designed and synthesized. The nine molecules were employed as the photosensitizing reagent in the fabrication of dye-sensitized solar cells and applied in photocatalytic water reduction via coupling with TiO_2 semiconductors and Pt co-catalyst. The highest turnover number (TON) of 10200 was achieved by organic photosensitizer **1g** for hydrogen generation. The effect of alkyl chains and triarylamine donor moiety to the photocatalytic performance was investigated. A shorter alkyl chain was found to favor the reaction due to a lower hydrophobicity which in turn may block the interaction between the photocatalyst and water molecules. Besides, the triarylamine donor units facilitated high hydrogen generation rates by reducing the contact between catalytic active sites and the oxidized form of sacrificial reagents.

In chapter 3, five earth-abundant metal complexes were synthesized to serve as the catalyst and CdS nanorods (NRs) were prepared to be the photosensitizer for the photocatalytic water reduction. A cobalt dithiolene complex (**2a**) achieved a TON of 30635 in 20 h under the blue light irradiation at a concentration of 10 μM. A new complex **2c** also gave a high TON of 12375 under the same conditions and its TON was further improved to 115213 in 87 h by reducing the concentration of

catalyst by ten times. The size effect of CdS NRs was investigated and larger nanoparticles exhibited higher hydrogen production rates. The accumulation of dehydroascorbic acid was proved to retard the photocatalytic reaction, thus providing a new perspective on the selection of sacrificial electron donor.

In chapter 4, ten iridium(III) complexes were synthesized and used as dual-functional molecules in photocatalytic carbon dioxide reduction by acting as both the photosensitizing reagent as well as the catalyst. The best performance was achieved by **3j**, giving a TON of 230 under the irradiation of blue LED. A push-pull effect brought by trifluoromethyl and methoxy group sucessfully enhanced the carbon dioxide reduction efficiency. The hydrophobicity of n-butyl chain also provided effective protection to the active sites of reaction intermediate. Additional steric hindrance was found to extend the lifespan of photocatalytic systems but led to a drop in the overall conversion efficiency.

Chapter 5 summarizes the specific synthetic procedures and characterization parameters of the molecules in chapters 2-4.

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