Studies on Electro- and Photo-catalytic Reduction of Carbon Dioxide

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論文内容の要旨

This dissertation focuses on the electro- and photo-catalytic reduction of carbon dioxide (CO_2) that is currently considered as one of possible approaches for storage of the solar energy in the form of chemical energy (artificial photosynthesis). The dissertation is divided into five chapters.

Chapter 1 gives a brief discussion on the energetic and environmental importance of converting CO_2 to valuable molecules and the reported precious and non-precious metal-based catalysts that showed high efficiency, product selectivity, and stability for converting CO_2 to CO. The mechanisms of the operation of these catalysts and comparison among these catalysts were also discussed. At the end of this chapter, the different photocatalytic methods for CO_2 reduction were discussed including the molecular and semiconductor approaches.

Chapter 2 describes our approach for modifying the well known $[Ru(bpy)_2(CO)_2]^{2+}$ as a CO_2 reduction catalyst with phosphonate tethers for binding to metal oxide electrodes and use the electrode/modified catalyst as efficient heterogeneous electrocatalyst for CO_2 reduction to CO. The synthesis, characterization and performance of the catalyst were discussed.

Chapter 3 describes the synthesis, characterization, and performance of new set of iron porphyrin dimers that show the best activity and stability for CO_2 reduction than any reported catatalysts. The dimer catalysts were designed to have a local pull-push mechanism, that is thought to enhance the catalyst activity in reported iron-porphyrin monomer studies. By comparison with the analogous iron porphyrin monomers used as a control experiment in this study, we demonstrate the importance of the dimer setup for the high catalytic performance. The author also studied the electronic effects of several aryl groups on the performance of these classes of catalysts, where electron-withdrawing groups on porphyrin periferal positions remarkably increase the catalytic efficiency upon CO_2 reduction to CO. The author also demonstrates the importance of the iron-iron separation in the dimer on their activity by comparison of an 1,2-phenilene linked dimer with the corresponding 1,3-phenylene one. The latter showed a lower activity than the 1,2-phenylene one and worked as two monomers.

Chapter 4 describes on the modification of the iron porphyrin dimer catalyst by a phosphonate tether to bind to the metal oxide electrodes and on the use the electrode/catalyst assembly as an efficient heterogeneous assembly for CO_2 reduction.

In chapter 5, integration of phosphonate modified $[Ru(bpy)_2(CO)_2]^{2+}$ as a CO_2 reduction catalyst with CuO is shown for the photocatalytic reduction of CO_2. The author chooses CuO as a p-type semiconductor, because it has a narrow band gap (1.4 eV), which is suitable for the will absorbance of a wide range of visible light. The synthesis of the *p*-CuO semiconductor and its properties were discussed. The integration of the catalyst with the semiconductor was also discussed. The performance of the catalyst/p-CuO was tested in a photoelectrochemical setup using the solar-simulator light of power 100 mW/cm^2.