SUMMARY OF Ph.D. DISSERTATION

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Title

Fabrication of precise metal-assembling polymers for nanocatalysts

Abstract

The conversion of small molecules, such as dioxygen and carbon dioxide, has attracted attention as the next generation's energy and material source. Because these reactions involve multi-electron transfer processes, the development of catalysts to process them is demanded. In this study, I have established the synthetic procedures of multinuclear metal complexes and metal-assembling polymers aiming at the fabrication of novel nanocatalysts, and have also evaluated their performances.

In chapter 1, metal complex catalysts for converting small molecules are described. I employed a dinuclear porphyrin complex which is known as a good catalyst for the four-electron reduction of dioxygen. The catalytic activity of the complex was electrochemically evaluated, and it was found that the carbon dioxide is effectively reduced with a cobalt porphyrin and the activity doubles by forming the dinuclear complex.

In chapter 2, I employed a cyclam complex which is known as a good catalyst for carbon dioxide. A novel phenylazomethine dendrimer having the cyclam core was synthesized, and it was found that the dendrimer showed a stepwise complexation on the dendron part. A precisely controlled hetero-metal complex was also constructed by forming a zinc cyclam complex at the core while the dendron coordinated with $SnCl_2$ or $AuCl_3$.

In chapters 3 and 4, fabrication of a metal nanoparticle catalyst is described. By using the metal assembling property, the phenylazomethine dendrimer is able to receive precursors of the metal nanoparticle with selective control of their number. After reduction or decomposition of the dendrimer metal complex, the metal nanoparticle of uniform size can be obtained.
In this research, I aimed at the fabrication of a Pt nanoparticle. Through pyrolysis of a dendrimer-$PtCl_4$ complex, I succeeded in obtaining a novel catalyst material which consisted of both a uniform Pt nanoparticle and a carbon material in one step. It was also confirmed that the Pt nanoparticle works as a catalyst for the dioxygen four-electron reduction by the modified electrode method. Photolysis was also used as a method to fabricate the Pt nanoparticle, and it was confirmed that it can produce the nanoparticles.

In Chapter 5, I designed a novel phenylazomethine dendrimer to improve the shell effect of the dendrimer. A tetraphenylmethane was employed as the core molecule because of its three-dimensional symmetry. The "dense-shell" structure of the synthesized dendrimer was confirmed by various measurements. Moreover, the Pt nanoparticle was also produced using this dendrimer by chemical reduction after complexation with $PtCl_4$, which worked as a good catalyst for the dioxygen reduction.

In summary, I synthesized several types of novel materials having highly controlled structures on a nanometer scale, and evaluated their performance as a catalyst for the conversion of small molecules, such as carbon dioxide or oxygen reduction.