博士論文の要約

論 文 題 目　Research on Covalent Organic Frameworks as a Materials Platform for Electrochemical Energy Storages
（電気化学的エネルギー貯蔵に向けた物質プラットホームとしての有機共有結合構造体の研究）

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Covalent organic frameworks (COFs) have attracted much attention as porous crystalline polymers with periodic structure, formed by robust covalent bonds. They have various advantages such as designable structures, controllable synthesis, and manipulative functions, which make COFs a promising materials platform for many applications. For instance, their porosity with large pore diameters and, open and straight channels, are beneficial to mass transportation; the manageable pores and hierarchical structures are able to facile the diffusion of molecules and ions. In addition, it is easy to tune their electronic structures by introducing functional building moieties such as electron donating/withdrawing groups in COFs. From this perspective, one of the most promising applications of COFs is to energy materials in solid-state electrochemistry, which is total science and technology of redox activity, adsorption and transport of electrons and ions, and etc. However, these applications have been prevented by the most significant drawback of COFs, namely their insulating property.

To address this issue, several approaches have been developed to increase the electrical conductivity of the COF-based electrode materials. Recently, several conductive COFs are prepared via bottom-up strategy from specific building blocks, though the variety of materials is limited. It is possible to increase the conductivity by making COF composites with conductive the improvement in conductivity is not very successful. Another very different approach is to pyrolyze COFs into porous heteroatom-doped carbons (PHCs), which are attracting much attention as promising electrode materials for supercapacitors. However, direct pyrolysis of COFs is found to result in significant collapses of the pores structures in the precursor COFs.

The present thesis work focuses on solving the problems in the approaches described above and on developing COF-derived electrode materials for electrical energy storages. In Chapter 1, COFs and their application to electrochemical energy storage are described. In the first part, the structures, variety, synthesis and general applications of the COFs are demonstrated in detail. In the second part, the application of COFs to electrochemical energy storages is discussed. In Chapter 2, to enhance the electrical conductivity of the COFs, we develop in-situ solid-state polymerization of a conductive polymer, poly(3,4-ethylenedioxythiophene) (=PEDOT) in the cavity space of a redox-active COF. The obtained PEDOT@COF exhibits an excellent electrical conductivity of 1.1 S cm^{-1}, which is higher than that of the parent COF by 9 orders of magnitude. In addition, PEDOT@COF electrodes exhibit remarkable performance as Faradaic and capacitive energy storages with specific capacitance of 1663 F g^{-1} at 1 A g^{-1}, fast charge/discharge rate performance of 998 F g^{-1} at 500 A g^{-1}, and excellent stability over 10,000 cycles. In Chapter 3, a salt-assisted pyrolysis of COFs is proposed to prepare porous PHCs. A pyrolysis of the COFs impregnated with K_2CO_3, which plays the role of a kind of foaming agent, results in PHCs with a hierarchical porous structure and an ultra-high specific surface area of up to 3451 m^2 g^{-1}. The supercapacitors of this material exhibit high specific capacitances of 1711 F g^{-1} at 1 A g^{-1} and 856 F g^{-1} at 500 A g^{-1} together with excellent stability. In Chapter 4, the salt-assisted pyrolysis strategy is optimized by using a dual-salt method, to regulate the porosity and the heteroatom concentrations in the PHCs. The electrochemical performance is systematically studied under the controls of these parameters. Chapter 5 summarizes the strategies for developing COF-derived electrode materials and their great abilities in the applications for electrochemical energy storages.