

論文 / 著書情報  
Article / Book Information

題目(和文)	
Title(English)	Control of Crystal Size and Microstructure of Three-Dimensional Covalent Organic Frameworks
著者(和文)	Wang Xiaohan
Author(English)	Xiaohan Wang
出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第12683号, 授与年月日:2024年3月26日, 学位の種別:課程博士, 審査員:村上 陽一,井上 剛良,花村 克悟,河野 正規,植草 秀裕
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第12683号, Conferred date:2024/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

# Control of Crystal Size and Microstructure of Three-Dimensional Covalent Organic Frameworks

WANG Xiaohan

This thesis consists of five chapters, as described below.

In Chapter 1 “Introduction”, typical porous materials and their typical utilities are summarized. Then, covalent organic frameworks (COFs) are described as an emerging category of porous materials. Structures, properties and representative applications of COFs are introduced in this chapter. Based on the description of applications envisaged in this thesis, present problems in COF formation and recent efforts to address them are listed. Specifically, (i) insufficient crystal quality and size, (ii) insufficient understandings on crystallization mechanism, (iii) lack of exploration of topological diversity, and (iv) lack of studies on 3D-COFs are proposed as the present issues that requires addressment. Therefore, this thesis aims to (i) discover governing factors on the crystal growth of 3D-COFs and elucidate the mechanism; (ii) construct a strategy to grow a 3D-COF with high crystallinity and large crystal size; (iii) expand topological diversity in the microstructure of 3D-COFs; (iv) acquire understandings on the application of 3D-COFs to thermal energy storage based on water vapor adsorption.

In Chapter 2 “Elucidation of factors that dictate crystal size and nucleation”, the necessity of improving the crystal size of 3D-COF crystals is explained. Then, the utilization of ionic additives was proposed as the strategy of this thesis. Specifically, a typical 3D-COF, COF-300, is chosen as subject, with the addition of systematically selected ionic additives into the COF crystal growth solution for investigating the impact of crystal size. As a result, the ranking of obtained COF crystal size is found to obey the Hoffmeister order and Guttmann donor number of ionic additives. Furthermore, using this strategy, COF crystals with sizes over 200  $\mu\text{m}$  are successfully generated, which is the largest single crystal reported for imine-based 3D-COFs to date. Finally, mechanism of the effect of ionic additives on nucleation of COF crystals is proposed as the dipole-dipole interactions between molecules in COF growth solution and ionic additives.

In Chapter 3 “Diversification of 3D-COF structures by generation of framework isomers”, the use of flexible building blocks is proposed as the strategy of improving the diversity of 3D-COF structures. Based on this motivation, two building blocks named as TAM and 4EBDA is chosen for developing 3D-COF. TAM is chosen due to its tetrahedral molecular structure and relatively flexible center junction. 4EBDA is chosen for the incorporation of tetraethylene glycol (TEG) side chains. By tuning the composition of crystal growth solution, the first example of 3D-COFs with triple framework

isomerism is discovered. These isomers are fully characterized and their structures are unambiguously determined by Rietveld refinement or single-crystal X-ray diffraction analysis. Through the characterizations, TK-COF-1, TK-COF-2 and TK-COF-3 are demonstrated to be framework isomers with identical chemical composition and different topologies of skeletons. Moreover, it is found that TK-COF-2 can be converted to TK-COF-3 in the crystal growth solution under specific conditions, which indicate that TK-COF-2 is a kinetic isomer. In contrast, TK-COF-3 is a thermodynamic isomer.

In Chapter 4 “Characterization of water adsorption and desorption properties of 3D-COFs used in this study”, water adsorption properties of 3D-COFs used in this thesis are elucidated. For COF-300, water adsorption properties are elucidated by the combination of water adsorption isotherm, thermogravimetric analysis, and differential scanning calorimetry. Then, water adsorption enthalpy is calculated based on the water adsorption isotherm. For TK-COFs, water adsorption properties of three isomers are elucidated by the measurement of water adsorption isotherm. Then, the causes behind the obtained results are discussed and the strategies for improving the water adsorption performance of 3D-COFs are proposed.

In Chapter 5 “Conclusion”, findings and achievements obtained in each chapter are summarized. In this thesis, (i) the influence of ionic additives on COF crystal size by impacting the nucleation of COF crystal growth is elucidated; (ii) an ionic additive strategy is developed to obtain 3D-COF crystals with large crystal size and high crystallinity; (iii) the first example of triple isomerism of 3D-COFs is discovered by using the strategy of flexible building blocks; (iv) water adsorption properties of 3D-COFs used in this thesis are elucidated and evaluated for the application of thermal energy storage based on water adsorption.