論 文 の 内 容 の 要 旨

生物材料科学　　　　専攻
平成29年度博士課程　　　　入学
氏 名　　　李 志強
指導教員名　　竹村　彰夫

論文題目　Study on metal-organic frameworks (MOFs) deposition onto cellulosic materials
(セルロース系材料への金属－有機構造体(MOF)の堆積に関する研究)

Chapter 1 General Introduction

Metal-organic frameworks (MOFs), a new class of porous crystalline materials composed of transition metal ions linked by polyfunctional organic linkers with coordination bond, have been drawn much attention over recent years due to their large surface area and adjustable pore size. Due to their excellent properties, MOFs have been widely studied for various applications, such as gas storage, separation, sensing, catalyst and antimicrobials. MOFs normally present as a form of powder, so for industrial application processes, it is essential to mold or form these crystalline powders to certain shapes for a specific use. Cellulosic materials derived from abundant plant resource have inherent advantages of low specific gravity, low cost, recyclability and biodegradability and many active chemical groups on the fiber surface. Therefore, the objective of this work is to study the metal-organic frameworks deposited onto cellulosic materials in term of green synthesis and optimum fabrication routes. The research and application of the MOFs functionalized cellulosic materials using the strategy investigated in this work will expand the high-value applications of cellulosic materials with the advantages of being more economical and environmental-friendly.

Chapter 2 Synthesis and characterization of Cu-BTC metal-organic frameworks onto lignocellulosic fibers by layer-by-layer method in aqueous solution

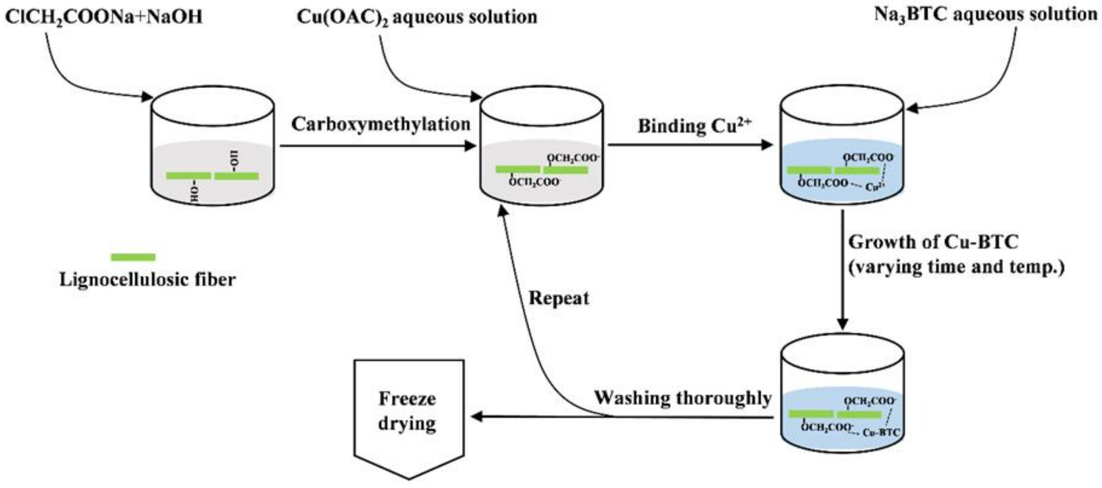

Fig. 1 Schematic of the preparation of Cu-BTC@CHFs in aqueous solution

In this chapter, the composites of Cu-BTC metal-organic framework onto high yield pulp fibers were prepared in aqueous solution using trimesic salts as linker sources for coordination bonding with copper, as shown in Fig. 1. The lignocellulosic fibers were first subjected to a carboxymethylation process for obtaining carboxyl group, then the Cu-BTC crystals depositing onto fibers were prepared by a layer-by-layer method and the synthesis temperature and time was also investigated. The as-prepared composites were further characterized by various techniques, such as ATR FT-IR, XRD, SEM, and specific surface area analyzer.

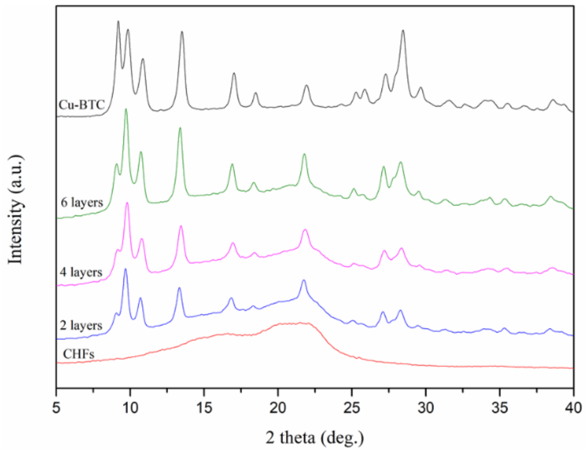

Fig. 2 XRD spectra of Cu-BTC, CHFs, and Cu-BTC@CHFs with different layers

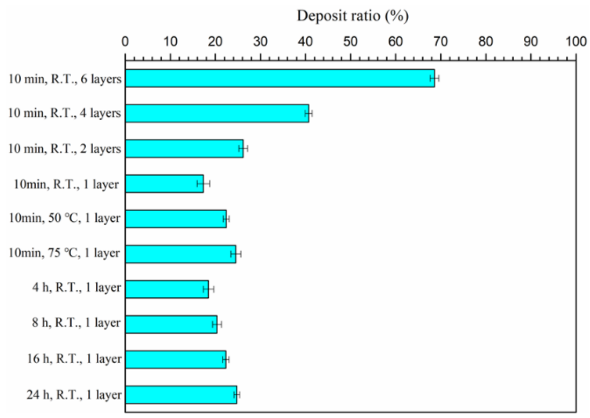

Fig. 3 Deposit ratio of Cu-BTC onto CHFs in different preparation condition and growth layers

The XRD patterns were shown in Fig. 2. More characteristic peaks of Cu-BTC were observed when increasing the growth layer, which overlapped with the peaks of CHFs. This can be attributed to more Cu-BTC depositing onto fiber surface and the formation of a thicker Cu-BTC film.

The deposit ratio increased slightly with raising growth temperature and extending growth time but increasing remarkably with more growth layers, as shown in Fig. 3. The specific surface area of synthesized Cu-BTC@CHFs had a significant promotion compared with unmodified fibers, showing a certain gas adsorption capacity, which can be further used as a porous material.

Chapter 3 A comparative study of depositing Cu-BTC metal-organic framework onto cellulosic filter paper via different procedures

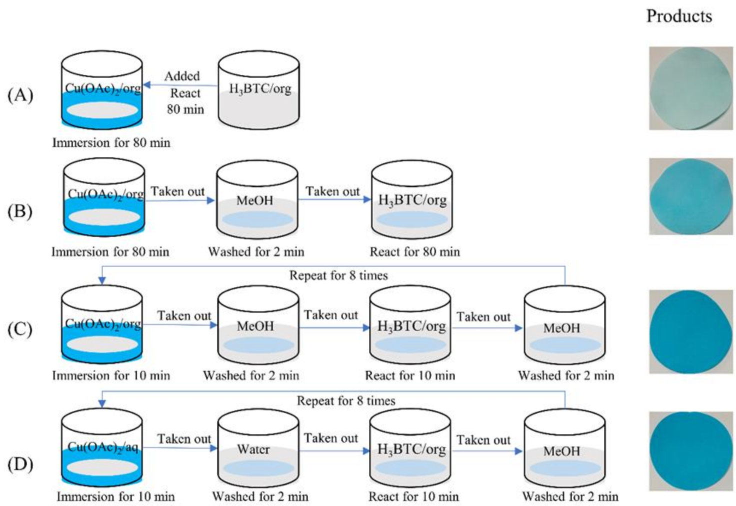

Fig. 4 Schematic of depositing Cu-BTC onto carboxymethylated filter paper in different procedures

In this chapter, the key characteristics and properties of Cu-BTC metal-organic frameworks deposited onto commercial filter paper prepared via four different procedures (one-pot, two-step, LbL-org, LbL-wtr-org) were comparatively studied, as shown in Fig. 4. The prepared products were characterized by SEM, EDS, ATR FT-IR, and XRD. The deposit ratio and gas adsorption capacity were also evaluated.

Table 3-2 Deposit ratio of Cu-BTC onto carboxymethylated filter paper prepared by different procedures

Procedures	Deposit ratio (%)
One-pot	1.31 ± 0.06
Two-step	4.23 ± 0.63
LbL-org	31.49 ± 3.46
LbL-wtr-org	39.38 ± 1.11

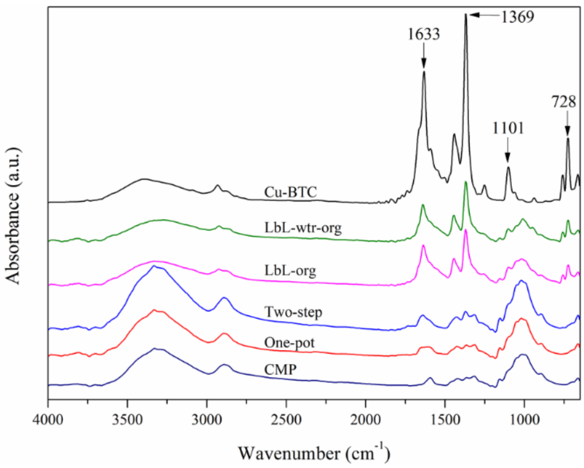

Fig. 5 ATR FT-IR spectra of CMP, Cu-BTC and Cu-BTC@CMP prepared by different procedures

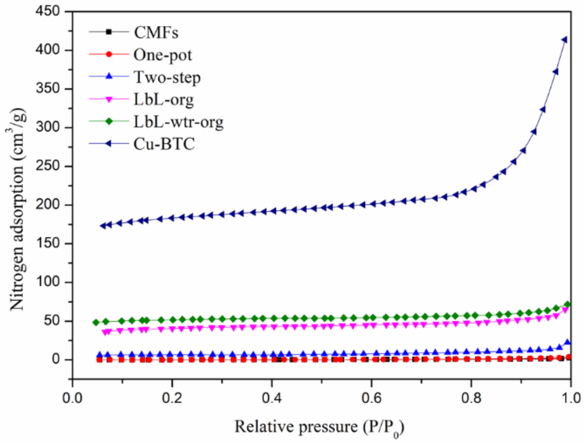

Fig. 6 Nitrogen adsorption isotherms of Cu-BTC, CMP, and Cu-BTC@CMP prepared by different procedures

The deposit ratio results in Table 3-2 showed that when using two-step procedure, the deposit ratio increased from 1.31% in the one-pot procedure to 4.23%, but a remarkable yield increase was achieved in layer-by-layer procedures, reaching up to 31.49% in LbL-org and 39.38% in LbL-wtr-org, respectively.

IR results shown in Fig. 5 suggest that Cu-BTC crystal deposited on carboxymethylated filter paper can be reinforced by a two-step preparation procedure and further enhanced remarkably by the LbL-wtr-org preparation procedure. The products prepared by the LbL-wtr-org procedure showed the highest gas adsorption capacity, as shown in Fig. 6, which will be an optimal pathway for the preparation of MOFs deposited onto cellulose-based material with the advantages of saving organic solvents and best gas adsorption ability.

Chapter 4 Overall Summary

Increasing the growth temperature and time would enhance the deposit of Cu-BTC onto fiber surface slightly, however increasing the growth layers would promote the deposit ratio significantly (from 26.2% to 68.6%, 2 layers to 6 layers). The specific surface area of synthesized Cu-BTC@CHFs had a distinct promotion compared with unmodified fibers, showing a certain gas adsorption capacity.

MOFs (Cu-BTC) were deposited onto carboxymethylated filter paper (CMP) using four different preparation procedures: one-pot, two-step, layer-by-layer-organic (LbL-org), and layer-by-layer-water-organic (LbL-wtr-org). The Cu-BTC crystals were found to grow in the main solution rather than on the substrate surface and the layer-by-layer method would contribute to a remarkable quantity of MOFs depositing onto the substrate surface. The LbL-wtr-org procedure will be an optimal pathway for depositing metal-organic frameworks onto cellulose-based materials with the advantages of saving organic solvents and best gas adsorption ability.

Chapter 5 Recommendations for future work

Growth of MOFs within the porous cellulosic materials, mechanical effect and mechanism after MOFs growth on the cellulosic substrates, and the specific applications of MOFs/Cellulosic materials composites based on different forms of cellulosic materials should be considered for future work.