Synthesis of Metal Organic Framework (MOF-199) Coated with Cellulose Nanocrystal

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Abstract: The hybrid material of a copper-based metal-organic framework (MOF-199) and cellulose nanocrystal (CNC) was explored in this research. A highly porous MOF-199 was synthesized from the reaction of copper nitratetetrihydrate and 1,3,5-benzenetricarboxylic acid by solvothermal method, and CNC was produced by combination method of chemical hydrolysis and mechanical treatment to reach high purity CNC with uniform shape. Physical characterizations of the MOF-199, CNC and MOF-199/CNC were achieved by using avariety of different techniques, including scanning electron microscope (SEM), transmission electron microscopy (TEM), BET surface area. Based on the results by coating CNC on the surface of MOF-199, the porosity of the product increases significantly.
***Keywords*:** Metal-organic framework, cellulose nanocrystal, BET surface area

INTRODUCTION

Metal–organic frameworks (MOFs) have attracted significant attention during the past decade due to several advantages such as high surface areas, tunable pore sizes, and the ease of processability, flexibility, and structural diversity [1–3]. On the other hand, cellulose is one of the most important natural polymers produced in the biosphere. Nanocellulose obtained from cellulose has two forms: cellulose nanofiber (CNF) and cellulose nanocrystal (CNC). CNC is reported to be stronger than steel and comparable to Kevlar. Due to its low density, it has a remarkably high strength over weight ratio. Also, its ''nano'' dimensions make it an ideal reinforcing material for many applications [4-5]. In this research, the MOF-199 coated with CNC was produced as a novel material, which has potential for many applications.

MATERIALS AND METHODS

In a typical preparation, a solid mixture of Cu(NO3)2.3H2O(0.438 g, 1.81 mmol) and 1,3,5-benzenetricarboxylic acid (H3BTC)(0.236 g, 1.12 mmol) was dissolved in a mixture of DMF (3 ml),ethanol (4 ml) and water (2 ml) in a 20 ml vial. The vial was heated at 85 ◦C in an isothermal oven for 24 h. The solid product was obtained by decanting with mother liquor and washed with DMF(24 ml).Solvent exchange was then carried out with ethanol (24ml) at room temperature. The product was then dried under vacuum at 170 ◦C for 6 h. Microcrystalline cellulose as initial material (20 g) was mixed with 300 mL sulfuric acid (63.5 %w/w) at 30 ºC, under mechanical stirring and ultrasonic treatment at 50 Hz for 6 h. Immediately, the suspensions were diluted using five times volume of distilled water to terminate the hydrolysis reaction. Then the suspensions were centrifuged at 12,000 rpm for 10 min, washed with distilled water for 3–4 times. The supernatant was removed from the sediment and replaced by distilled water after each washing. The suspension was then placed in dialysis tubes having a molecular weight cutoff of 12,000–14,000 to remove free acid and dialyzed against distilled water for several days until the suspension reached neutrality. For preparing MOF-199 coated with CNC, 0.04 g CNC+1ml H_2O was added into the Cu(NO3)2.3H2O and then followed the reaction of MOF-199 production.

RESULTS AND DISCUSSION

The SEM and TEM images in Fig. 1 depict the morphology of the MOF-199, CNC and MOF-199 coated with CNC, respectively.

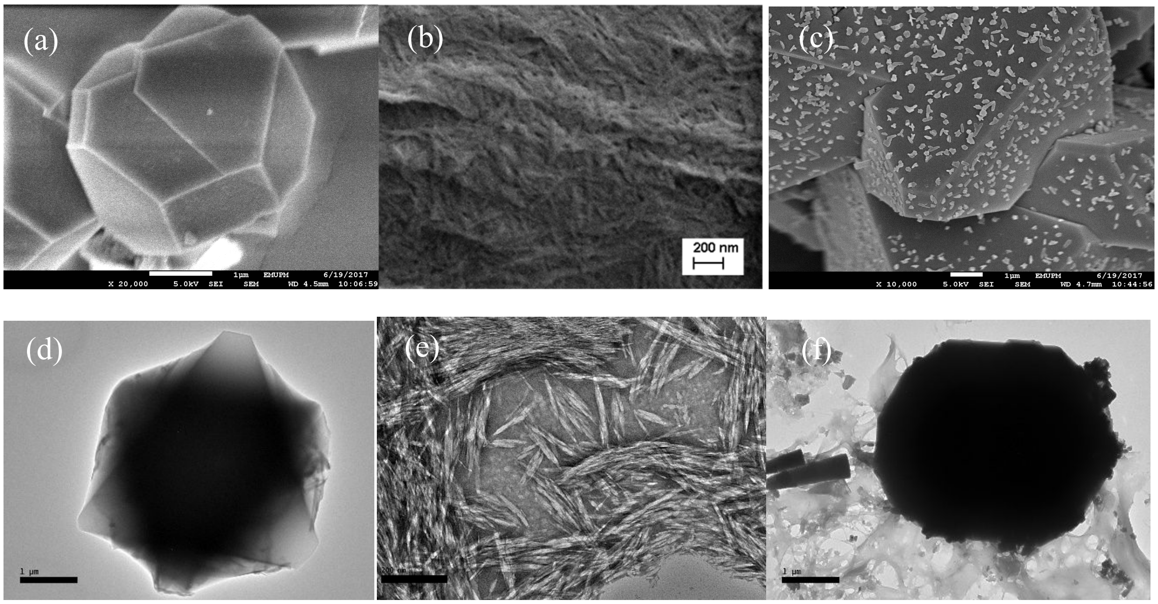

Fig. 1. (a-c) SEM images of MOF-199, CNC and MOF-199/CNC, (d-f) TEM imagesof MOF-199, CNC and MOF-199/CNC.

According to the images, CNCs present a needle-like structure with uniform shape and an average length of 150 nm and a diameter of 12 nm (Fig.1 and 2). Besides, the SEM micrographshowed that a crystalline and hexagonal material of MOF-199 was achieved. Presence of CNC on the surface of MOF-199 indicates the orderly coating of CNC. BET surface area of MOF-199 was about 850m^2/g and for CNC is about 13.4 m^2/g. Although, the BET surface area of CNC is not remarkable, by coating the CNC on the surface of MOF-199, the porosity of MOF-199 increases, significantly to 1040 m^2/g.

CONCLUSIONS

In this research, MOF-199 coated with CNC was produced. The main important challenge of this research is related to improve the porosity of MOF-199 by coating the CNC with low BET surface area. Based on the results, coating uniformly of CNC with low BET surface area leads to improve the porosity of MOF-199, significantly.

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