



Capillarity-induced selective ex-situ synthesis of metal–organic framework inside mesoporous nanotubes



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ABSTRACT

A general synthetic strategy to confine metal–organic frameworks (MOFs) selectively and evenly inside lumen of mesoporous nanotubes is presented. This process includes even loading of a precursor for MOF among the nanotubes in a solution phase, and following ex-situ solvothermal reaction while the precursor is suspended exclusively inside the lumen of the nanotube by capillary action, where the nanotube acts as a template as well as an ultra-small vial. The hybrid exhibits unique gas adsorption behavior, in which both microporosity and mesoporosity exist simultaneously. Confining environment of the nanotube results in a preference of the growing MOF to a specific growth direction. Enhanced water stability of inner MOF is also observed.

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1. Introduction

Metal–organic frameworks (MOFs) are a class of highly micro-porous materials formed from metal ions or metal ion clusters linked by organic multivalent ligands to extend the structure three dimensionally. Since the first systemized synthesis of MOFs by O. M. Yaghi [1], hundreds of different MOFs have been reported with varying applications, including drug delivery systems (DDS), carbon dioxide capture (CDC), and hydrogen gas storage for fuels [2–4].

Some researchers have attempted to synthesize MOFs inside mesoporous materials, such as carbon nanofibers (CNFs) [5], SBA-15 [6], and silica monoliths [7]. In these cases, the intrinsic properties were significantly enhanced such as having an enlarged surface area compared with the original; increased stability towards water or other chemicals; change in growth direction, probably because of confined crystal growth; or enhanced catalytic activities for specific organic reactions.

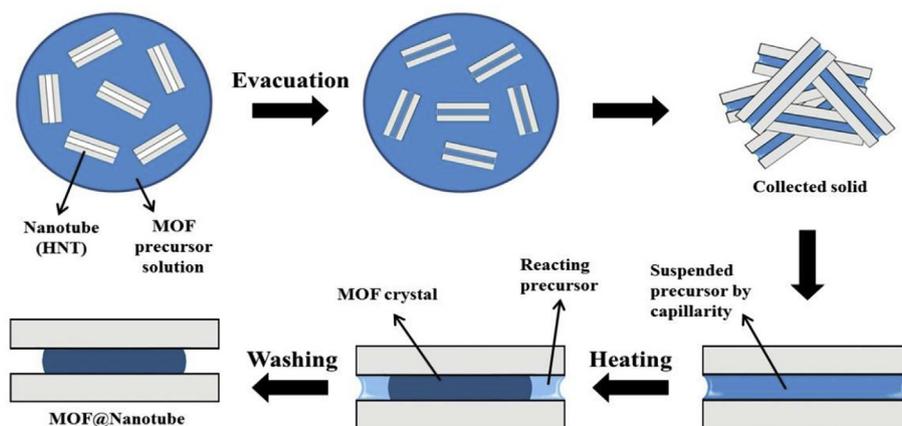
However, problems often arise with purifying or isolating the combined material from the unused template and the isolated bulk crystals after synthesis. For example, P. Pachfule et al. successively centrifuged and washed to isolate MOF-5@CNF when synthesizing MOF-5 inside CNF pores [5]. Even though purification

was possible because of the relatively large difference in density between the MOF-5 crystals and the MOF-5@CNF, the washing steps were time consuming and did not guarantee complete purification. It is also difficult to attain the even loading of MOFs among the pores. C. Wu et al. avoided the purification problem by shortening reaction time during the MOF-5 synthesis in the presence of SBA-15 [6], but the resultant crystals were not evenly distributed among the pores of SBA-15. Moreover, in order to attain encapsulation of MOF in mesoporous template, particular functional groups on the inner surfaces of the template were employed [5,8,9]. Since these problems lead to a substantial decrease in net efficiency of the product, it is crucial to establish an effective synthetic procedure.

All of these problems can be attributed to the inherent limitations of an in-situ solvothermal process. Thus, here we present a novel ex-situ synthetic method to confine MOFs exclusively and evenly inside the lumen of mesoporous nanotubes, while overcoming the aforementioned problems through the capillarity of the nanotube. The even loading of a MOF precursor among the nanotubes is carried out by a vacuum process in solution phase, and solvothermal synthesis is followed in ex-situ fashion, where the nanotube acts as a template as well as an ultra-small vial. The precursor is retained exclusively inside the lumen by the capillarity of the nanotube during the reaction, as depicted in Scheme 1. We also explore novel properties of the hybrid derived from the synergic interaction.

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Scheme 1. Synthetic process for MOF@Nanotube. Note that the reaction is carried out in ex-situ fashion.

In this study, we choose HKUST-1, an MOF consisting of copper ion clusters linked by a trivalent organic linker, trimesic acid, and halloysite nanotube (HNT) as a template. Hereafter the resultant hybrid will be called HKUST-1@HNT.

HNT is a 1:1 ratio aluminosilicate multi-walled nanotube similar in constitution to kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. It has cylindrical structure with a large surface area similar to a paper towel roll. The morphology is analogous to that of multi-walled carbon nanotube (MWNT) because it has a similar structure and scale. HNT has different functionalities at the inner and outer surfaces, with the outer surface being siloxane (Si–O–Si) and the inner aluminol (Al–OH). These structural differences are often used in applications such as drug delivery systems (DDS) and biomedical agents [10,11]. The lengths of HNTs along the longitudinal axis vary from 500 to 2000 nm, and the inner diameter ranges from 15 to 30 nm, as illustrated in Fig. 1.

2. Experimental

2.1. Materials and methods

Purified hydrated HNT was provided by Applied Minerals Inc., USA. Copper nitrate trihydrate (Daejung, above 99%), 1,3,5-benzenetricarboxylic acid (BTC, Lancaster, 98%), methanol (Daejung, above 99.8%), dimethyl sulfoxide (DMSO, Daejung, above 99.5%) were used without further purification.

Powder X-ray diffraction (XRD) pattern was collected on a D/MAX RINT 2000 with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The diffraction pattern was recorded at a scanning rate of $2^\circ/\text{min}$ from 3° to 40° . Transmission electron microscope (TEM, JEOL JEM-2100F) images were taken for the bare HNT and HKUST-1@HNT with operation voltage of 200 kV. A drop of sample (0.1 mg/mL) was placed on a 200-mesh copper Formvar carbon coated TEM grid.

Energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments) for HKUST-1@HNT was carried out right after the completion of the synthesis. Contrary to the previous TEM sampling method, the HKUST-1@HNT powder was directly transferred to a grid. To avoid any confusion over the EDS analysis, Nickel Formvar carbon film was used for EDS measurement. Nitrogen adsorption–desorption isotherms of each sample were measured by a volumetric gas adsorption instrument (BEL JAPAN Inc., BELSORP-Mini II).

The Brunauer–Emmett–Teller (BET) method was used to obtain total specific surface area and pore volume of each sample, and the Barrett–Joyner–Halenda (BJH) method was used to measure the samples' meso/macropore size distributions together with each pore volume and surface area. Relative pressure of 10^{-4} to 0.99 was applied and the operation temperature was 77 K. The samples were activated by evacuation while heating at 433 K before each measurement.

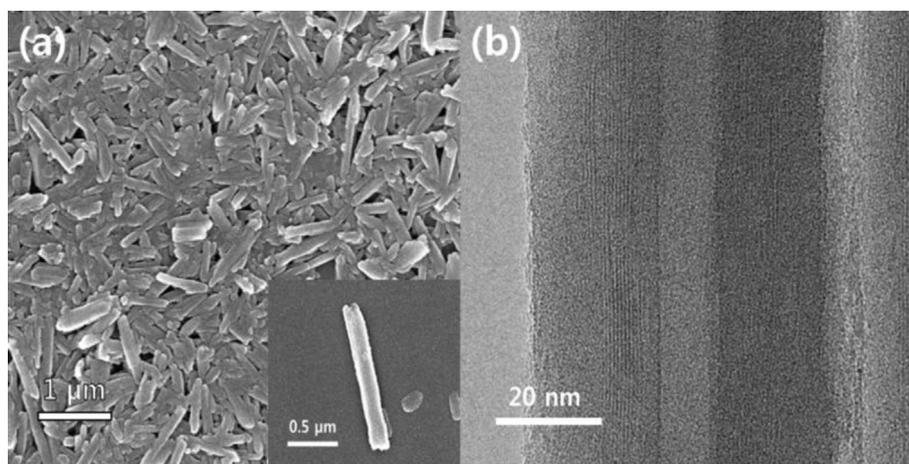


Fig. 1. Electron microscope images of halloysite nanotube (HNT). (a) SEM image and (b) TEM image. Inset in (a) represents single HNT observed by SEM.

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