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On the direct synthesis of Cu(BDC) MOF nanosheets and their performance in mixed matrix membranes

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ABSTRACT

High aspect-ratio nanosheets of metal-organic frameworks (MOFs) hold promise for use as selective flakes in gas separation membranes. However, simple and scalable methods for the synthesis of MOF nanosheets have thus far remained elusive. Here, we describe the direct synthesis of Cu(BDC) (BDC^{2-} = 1,4-benzenedicarboxylate) nanosheets with an average lateral size of 2.5 µm and a thickness of 25 nm from a well-mixed solution. Characterization of the nanosheets by powder and thin film X-ray diffraction, electron microscopy, and electron diffraction reveals pronounced structural disorder that may affect their pore structure. Incorporation of the Cu (BDC) nanosheets into a Matrimid polymer matrix results in mixed matrix membranes (MMMs) that exhibit a 70% increase in the CO_2/CH_4 selectivity compared with that of Matrimid. Analysis of new and previously reported permeation data for Cu(BDC) MMMs using a mathematical model for selective flake composites indicates that further performance improvements could be achieved with the selection of different polymers for use in the continuous phase.

1. Introduction

Metal-organic frameworks (MOFs) are a class of crystalline porous materials with a wide range of pore sizes and functionalities that render them attractive for a variety of potential applications [1,2], including catalysis [3,4], gas storage [5,6], and separations [7–9]. Particularly, certain MOF-based membranes are considered for separation of carbon dioxide from natural gas and flue gas streams [10,11].

Recently, membranes based on zeolite nanosheets were reported to exhibit unprecedented separation performance (high flux and selectivity) [12,13], which motivated the synthesis of MOF nanosheets and exploration of their uses in membrane applications [14–17]. As with other molecular sieve membranes [18], MOF nanosheet-based membranes are typically prepared either by (i) forming intergrown deposits of MOF nanosheets on porous supports in an effort to obtain the intrinsic separation properties of the nanosheets [14,17], or (ii) incorporating the nanosheets in polymer matrices to form mixed matrix membranes (MMMs) [15] that surpass the Robeson upper bound for polymeric membrane performance [19]. It has been convincingly argued that, from a manufacturing standpoint, the MMM approach is advantageous because it can be readily integrated with existing technologies for forming polymeric membranes [20–22]. Moreover, nanosheet-based MMMs can in principle achieve similar improvements in performance at lower loadings compared to MMMs formed with isotropic crystals [23–26].

The strategies employed for the synthesis of MOF nanosheets can be categorized into: (i) a top-down approach involving exfoliation of layered precursors using techniques such as sonication and ball-milling [14,27], or (ii) a bottom-up approach where crystal growth of MOFs having a tendency to grow anisotropically is tuned to favor the formation of plate-like morphologies by restricting growth along the preferred thin direction either via the adsorption of surfactant-like molecules [16] or by altering the manner in which metal and linker ions come into contact with each other [15]. As recently demonstrated for zeolite nanosheets, the bottom-up approach can often be more advantageous, not only because of its simplicity and higher yields, but also in terms of improved nanosheet quality enabling significantly better membrane performance [28].

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Building on an earlier report that required nanosheet crystallization in a three-layer (linker-solvent-metal) gradient [15], we report here the bottom-up synthesis of Cu(BDC) nanosheets by direct homogeneous mixing of the metal and linker solutions. We find that it is possible to tune the aspect-ratio of the nanosheets by varying the synthesis temperature, and carry out detailed structural characterization using electron microscopy and X-ray diffraction. Mixed matrix membranes are successfully fabricated by incorporating the nanosheets into a polymer matrix. We obtain effective permeabilities for the Cu(BDC) nanosheets from permeation data and analyze the MMM performance using a mathematical model.

2. Experimental

2.1. Chemicals

Anhydrous *N*,*N*-dimethylformamide (DMF, 99%), terephthalic acid (H_2BDC, 98%) and copper nitrate trihydrate ($Cu(NO_3)_2$, 99%) were obtained from Sigma Aldrich. Acetonitrile (CH_3CN, 99.9%), and chloroform ($CHCl_3$, 99.9%) were obtained from Fisher Scientific. Matrimid 5218 was provided by Huntsman Advanced Materials and was degassed at 180 °C under reduced pressure (0.1 bar) for 16–18 h. Chloroform was filtered using a 0.2 µm PTFE syringe filter (Pall Corporation). All other chemicals were used as received.

2.2. Direct synthesis of Cu(BDC) nanosheets

2.2.1. Direct synthesis – no mixing

The metal solution was prepared in a glass vial by adding 1 mL of DMF and 3 mL of CH_3CN to 30 mg of $Cu(NO_3)_2$. The linker solution was prepared by adding 3 mL of DMF and 1 mL of CH_3CN to 30 mg of H_2BDC. The metal solution was added in one portion to the linker solution and the resulting mixture was left to stand at ambient temperature. After 24 h, the solution was centrifuged to obtain Cu(BDC) nanosheets that were then washed 3× in DMF. The nanosheets were stored by suspending them in DMF.

2.2.2. Direct synthesis – gentle mixing with shaker

Typically, the metal solution was prepared in a conical flask by adding 30 mL of DMF and 90 mL of CH_3CN to 900 mg of $Cu(NO_3)_2$ while linker solution was prepared by adding 90 mL of DMF and 30 mL of CH_3CN to 900 mg of H_2BDC. The metal solution was then added dropwise to the linker solution over a period of 40 min under magnetic stirring. After complete addition, the resulting solution mixture was shaken in an orbital shaker (Thermo Scientific MAXQ 4000) at a speed of 200 rpm under a constant temperature (15 °C, 25 °C, or 40 °C). After 24 h at the set temperature, the solution was centrifuged to obtain Cu (BDC) nanosheets, which were then washed 3× in DMF. A suspension of the Cu(BDC) nanosheets in DMF was then solvent exchanged in chloroform by repeated centrifugation. The supernatant was discarded each time and ~ 40 mL of fresh chloroform was added to the sediment (corresponding to ~ 2.5 mg of wet nanosheet cake per mL of chloroform). The cake was dispersed by vortexing (Fisher Scientific vortex mixer) for ~ 5 min, sonicated (Branson 5510R-DTH ultrasonic cleaner) for ~ 15 min, and then centrifuged. This process was repeated 3×. The nanosheets thus suspended in chloroform were eventually used for the fabrication of MMMs.

2.3. Characterization of Cu(BDC) nanosheets

2.3.1. X-ray diffraction (XRD)

After washing in DMF, the cake of Cu(BDC) nanosheets was oven dried at 70 °C. The dried as-synthesized powder was then added to a polyimide capillary (Cole-Parmer, 0.0395 in. inner diameter × 0.0435 in. outer diameter, 0.6 in. in length) that was then sealed at both ends. X-ray diffraction measurements were performed at beamline 17-BM at the Advanced Photon Source, Argonne National Laboratory (APS, ANL). A Perkin Elmer amorphous silicon flat panel detector was used to acquire two-dimensional diffraction patterns with program QXRD. The data were converted to traditional xy files of intensity versus 2θ using the GSAS-II program [29]. The X-ray wavelength was 0.24119 Å. Values of 2θ were correspondingly converted to Cu-Kα radiation.

For out-of-plane X-ray diffraction, a suspension of nanosheets in DMF was drop-cast onto a porous silica support [28] to obtain an oriented coating. Out-of-plane X-ray diffraction measurements were performed at Beamline 33-BM-C at APS, ANL using a source wavelength of 0.77493 Å. After converting 2θ values to Cu-Kα radiation, the data were processed using MDI-JADE 2.6.5 software.

Cu(BDC) nanosheets, solvent exchanged in chloroform, were characterized using in-plane X-ray diffraction. The sample was prepared by depositing nanosheets suspended in chloroform onto porous silica supports by vacuum filtration. In-plane measurements were performed at Beamline 33-BM-C at APS, ANL using a source wavelength of 0.77493 Å, and 2θ values were correspondingly converted to Cu-Kα radiation. The data were processed to subtract a linear background using MDI-JADE 2.6.5 software.

2.3.2. Scanning electron microscopy (SEM)

SEM analysis was performed using JEOL 6700 and Hitachi SU8230 scanning electron microscopes. An accelerating voltage of 1.5 kV was used with the JEOL 6700 equipped with a field emission gun. The Hitachi SU8230 was operated in the deceleration mode at a landing voltage of 0.8 kV. Samples for SEM analysis were prepared by drop casting the nanosheet suspension onto a Si wafer.

2.3.3. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED)

A FEI-Tecnai T12 TEM with LaB_6 filament gun operating at 120 kV and equipped with a Gatan MSC794 CCD camera was used for TEM imaging and SAED. Cu(BDC) nanosheets were transferred from suspensions onto lacey carbon films supported on 400 mesh copper grids, and the solvent was allowed to evaporate before TEM analysis. Simulated electron diffraction patterns were obtained using the Single Crystal 2.3 software. Radial averaging of electron diffraction pattern was performed using a MATLAB code to determine the center of the ED pattern, followed by radial averaging of the peak intensity in reciprocal space. A line scan (*counts vs* 2θ after exponential background subtraction), starting from the center of the radially averaged ED pattern, was plotted for comparison with the X-ray diffraction pattern.

2.3.4. Atomic force microscopy (AFM)

A Bruker Nanoscope V Multimode Scanning Probe Microscope was used in tapping mode in the repulsive regime for collecting AFM images. A silicon nitride tip was used, and AFM images were collected at a scan rate of 0.8 Hz and 512 lines/scan. Samples for AFM analysis were prepared by drop casting the nanosheets suspension on a Si wafer. Gwyddion 2.4 software was used to analyze AFM images.

2.3.5. Annular dark-field scanning transmission electron microscopy (ADF-STEM)

Samples for ADF-STEM characterization were prepared by drop-casting a suspension of Cu(BDC) nanosheets onto an ultrathin carbon film on holey carbon support film (400 mesh Cu, from Ted Pella) and allowing the sample to air dry at room temperature. ADF-STEM images were acquired using aberration-corrected FEI Titan 60–300 (S)TEM, equipped with SuperX EDX detector, operating at 60 kV, with a 214 mrad electron probe convergence angle and 30 mrad ADF detector inner angle. The acquired ADF-STEM image was filtered by selecting the spots in Fast Fourier Transform (FFT) of the original image, followed by inverse FFT operation to generate a real space image.

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