# Patterning, Transfer, and Tensile Testing of Covalent Organic Frameworks Films with Nanoscale Thickness

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**ABSTRACT:** Covalent organic frameworks (COFs) are promising materials for a variety of applications including for membranebased separations, thin film electronics, and as separators for electrochemical devices. Robust mechanical properties are critical to these applications, but there are no reliable methods for patterning COFs or producing free-standing thin films for direct mechanical testing. Mechanical testing of COFs has only been performed on films supported by a rigid substrate. Here, we present a method for patterning, transferring, and measuring the tensile properties of free-floating nanoscale COF films. We synthesized COF powders by condensation of 1,3,5-tris(4-aminophenyl)benzene (TAPB) and terephthalaldehyde (PDA) and prepared uniform thin films by spin casting from a mixture of trifluoroacetic acid (TFA) and water. The COF films were then reactivated to recover crystallinity and patterned by plasma etching through a polydimethylsiloxane (PDMS) mask. The films were transferred to the surface of water, and we performed direct tensile tests. We measured a modulus of approximately 1.4 GPa for TAPB-PDA COF and a fracture strain of 2.5%, which is promising for many applications. This work advances the development of COFs for thin film applications by demonstrating a simple and generally applicable approach to cast, pattern, and transfer COF thin films and to perform direct mechanical analysis.

#### INTRODUCTION

Covalent Organic Frameworks (COFs) are crystalline, porous organic materials with well-defined pores, tunable architectures, and versatile chemistries.<sup>1</sup> They have been used in a wide range of applications including catalysis,<sup>2</sup> energy storage,<sup>3</sup> electronics,<sup>4</sup> and molecular separations.<sup>5</sup> COFs are typically produced in powder form and are insoluble in most solvents,<sup>6</sup> however, recent studies have produced COF thin films for various applications, such as electronic devices, membrane-based separations, and sensors.<sup>4-7</sup> For example, Wang et al. fabricated robust ambipolar vertical organic fieldeffect transistors using COF films grown on single layer graphene.<sup>4</sup> Banerjee and co-workers prepared self-standing porous COF films with micro-meter thickness through a simple slow annealing method. The resulting films exhibited excellent stability and could be used to separate gold nanoparticles from solution.8 Marder and coworkers synthesized a series of COF films with dihydroxy moieties and utilized those stable films as a colorimetric humidity sensor that quickly responded to water vapor.7

The mechanical properties of COF films are important for these applications<sup>9</sup>. However, only a few studies have attempted to analyze the mechanical behavior of COF thin films. Feng and coworkers<sup>10</sup> used "the strain-induced elastic buckling instability for mechanical measurements" for testing the modulus of a monolayer, two-dimensional polymer on an elastomeric

polydimethylsiloxane (PDMS) support.<sup>10</sup> Hao *et al.* and Chen *et al.* studied the Young's modulus of COF films using atomic force microscopy (AFM) on patterned silicon substrate and non-patterned flat silicon substrate, respectively.<sup>11,12</sup> Very recently, Fang *et al.* studied deformation and fracture of COF films using an *in situ* scanning electron microscopy (SEM) testing technique.<sup>13</sup>

Typically, standard tensile testing methods of thin films include direct tests of free-standing films without a substate<sup>14,15</sup> or indirect measurements of films on patterned substrate with holes.<sup>10,16,17</sup> Direct tests can provide information directly, without the need for additional analysis. However, it is difficult to prepare free-standing films without any cracks or defects, especially when the thickness is below 100 nanometers.<sup>18</sup> Although indirect tests provide a simpler procedure, interpretation of these tests is not straightforward and requires making several approximations related to the deformation of the material.<sup>18,19</sup> Another drawback of indirect testing methods is that the focus on a small region of the sample that may not reflect the properties of the entire film.

Herein, we report a floating film technique to directly measure the tensile strength of ultrathin COF films on water. We synthesized a COF by polycondensation of 1,3,5-tris(4aminophenyl)benzene (TAPB) and terephthalaldehyde (PDA) via a solvothermal synthesis route. We then prepared uniform and thin TAPB-PDA COF films by spin coating using



**Figure 1.** (a) Experimental PXRD and simulated PXRD of TAPB-PDA COF. (b) FTIR spectra of TAPB-PDA COF and starting monomers (blue: TAPB-PDA COF; red: PDA; black: TAPB). (c) Nitrogen adsorption and desorption isotherms. (d) Pore size distribution of TAPB-PDA COF. (e) SEM, scale bar =  $5 \mu m$  and (f) TEM images of TAPB-PDA COF, scale bar = 20 nm.

trifluoroacetic acid (TFA) and water as a solvent and patterned the COF films by plasma etching using a PDMS mask. The COF film was then lifted off and tested directly on the surface of water. Our tensile tests show that TAPB-PDA COF has a Young's modulus of approximately 1.4 GPa and a strain-tobreak of approximately 2.5%. This work demonstrates a simple approach to directly measure the tensile properties of freefloating COF films and to cast, pattern, and transfer COF thin films.

#### RESULTS AND DISCUSSION

TAPB-PDA COF was synthesized by polycondensation of 1,3,5-tris(4-aminophenyl)benzene (TAPB, 21 mg, 0.06 mmol) and terephthalaldehyde (PDA, 12 mg, 0.09 mmol) via a typical solvothermal method<sup>20</sup> (a mixture of 2 ml 1,4-dioxane and mesitylene, 4/1, v/v, 6M acetic acid, 120 °C, 3 days; Figure S1, Supporting information). Detailed synthesis procedures are provided in the Experimental Section. After synthesis, the dry framework powders were isolated after thorough solvent washing and dried using supercritical CO<sub>2</sub>.

TAPB-PDA COF was characterized by powder X-ray diffraction (PXRD) analysis, Fourier transformation infrared spectroscopy (FTIR), nitrogen sorption analysis, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). PXRD results (Figure 1a) were consistent with previous studies<sup>21</sup> and in excellent agreement with the simulated AA stacking model (Figure S2). The diffraction peak at 2.88° could be assigned to <100> reflection, while the peaks at 5°, 5.7°, 7.5°, and 10° corresponded to <110>, <200>, <210>, and <220> hexagonal reflections<sup>21</sup>, respectively. FTIR analysis

(Figure 1b) revealed the expected imine C=N stretching peak at 1619 cm<sup>-1</sup> appeared and that the aldehyde peak at 1681 cm<sup>-1</sup> was attenuated,<sup>21,22</sup> consistent with the polycondensation reaction to produce TAPB-PDA. TAPB-PDA COF exhibited a very high Brunauer-Emmett-Teller (BET) surface area (2240 m<sup>2</sup> g<sup>-1</sup>, surface area calculation plot is given in Figure S3), measured through nitrogen adsorption and desorption test (Figure 1c). The isotherm exhibited typical features of type-I isotherm curve. At the low-pressure range  $(P/P_0 < 0.01)$ , the absorbed amount of nitrogen increased rapidly, indicating a microporous structure. The pore size distributions (Figure 1d) were calculated using non-local density function theory (NLDFT) and predicted an average pore diameter of around 2.7 nm. SEM analysis (Figure 1e) indicated that this COF was comprised of macro-size spheres, and crystalline features are apparent in images obtained by high-resolution TEM (HRTEM) analysis (Figure 1f).

TAPB-PDA COF film was fabricated following a modified solvent processing approach<sup>6</sup> using spin coating followed by reactivation (Figure 2a). This process involved dissolving the COF in a mixture of TFA and 5% v/v water, followed by reactivation in the presence of an organic base to deprotonate the COF and recover crystallinity. Briefly, a desired amount of TAPB-PDA COF powder was fully dissolved in 1 mL of TFA containing 5% v/v H<sub>2</sub>O at room temperature and sonicated until it is fully dissolved (Figure S3). Then, the COF solution was spin coated (~2000 rpm) onto pre-cleaned and UV-ozone treated glass slide. UV-ozone treatment was necessary to



**Figure 2.** (a) Schematic for solution processing to produce COF thin films. (b) COF film thicknesses obtained from AFM measurements. (c) SEM image of spin coated film (2000 rpm) before deprotonation and reactivation, scale bar = 400  $\mu$ m. (d) SEM image of spin coated film after protonation and reactivation, with some small wrinkles visible in the film, scale bar = 100  $\mu$ m. (e) PXRD and (f) FTIR of different COF samples (black: pristine COF powders from direct synthesis; red: powders dried from COF/TFA/H<sub>2</sub>O solution; powders precipitated from COF/TFA/H<sub>2</sub>O solution after deprotonation and reactivation). (g) TEM image of powders precipitated from COF/TFA/H<sub>2</sub>O solution after deprotonation and reactivation). (g) TEM image of

produce uniformly coated films on glass (Figure S4). We were unable to produce uniform films on an Si wafer using a similar approach (Figure S5), possibly due to the hydrophobicity of the Si surface. We used a spin speed of 2000 rpm to deposit the films and studied different solution concentrations ranging from 16 mg ml<sup>-1</sup> to 128 mg ml<sup>-1</sup> to vary the thickness of the COF films. The spin-coated films were activated by immersion in triethylamine followed by thorough washing in water and methanol, and the color of the films changed from reddish to yellow due to the deprotonation of imine bonds. We were able to generate uniform films for all solution concentrations tested (Figure S4), and the thicknesses of the dried films ranged from 41 nm to 340 nm, as determined by AFM (Figure 2b, Figures S6-S10). SEM analysis (Figure 2c, d) showed little change of morphology for the as-prepared COF films before and after activation. In order to confirm that TFA/H2O dissolution did not completely destroy the crystalline structure of COFs, PXRD, FTIR and TEM tests (Figure 2e-g) were conducted to analyze the pristine as-synthesized COF powders as well as TFA/H<sub>2</sub>O treated powders before and after reactivation. While PXRD

analysis (Figure 2e) showed that TFA/H<sub>2</sub>O treatment reduced the crystallinities of COFs possibly due to the dynamic chemistry and partial decomposition of imine bonds,<sup>6</sup> the final COF powders were crystalline. The FTIR spectra (Figure 2f) after the powder reactivation was identical to the pristine COF, and HRTEM (Figure 2g) revealed clear crystalline lattice structure for the COF powders after reactivation. However, we did not observe crystallinity for the spin cast films as evidenced by the grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements acquired using a synchrotron X-ray source (Figure S12), possibly due to the fast evaporation of TFA during the casting process which can exert significant capillary forces that lead to pore collapse and irreversible loss of crystallinity. The FTIR spectrum of the spin coated film had almost identical features as that of the COF powder (Figure S13), indicating the chemistry of the spin coated film kept unchanged.



Figure 3. Preparation and transfer procedures of testing films with dog-bone shape



**Figure 4.** Tensile test of COF films. (a) Schematic of the testing device; (b) dog-bone shaped COF film attached to holder; (c) fracture of COF films; (d) stress-strain curve of COF film; (e) elastic modulus of COF films after three-times tests; (f) summary of elastic modulus of some polymeric materials.

The process of preparing COF film for mechanical testing is illustrated schematically in Figure 3. We first prepared a COF film on glass, as described in the earlier section. Next, a PDMS mask in the shape of a dog-bone was placed over the film for patterning. More details on the preparation of the PDMS mask are provided in the Experimental Section and Figure S14. The sample was then exposed to oxygen plasma, and the PDMS cover protected the underlying COF film, resulting in a dogbone shaped COF film after etching. After removal of the PDMS cover, the protonated COF films were carefully immersed in triethylamine, water, and methanol sequentially to deprotonate and reactivate the COF films. Before reactivation, the protonated COF films remained firmly attached to the glass slide, and the COF film was hydrophilic (see Figure S15a). However, after deprotonation under basic conditions and reactivation by methanol, the COF was hydrophobic (Figure S15b). After reactivation, the COF easily lifted off of the glass surface when placed in water. Tensile tests were performed on these free-floating COF films.

The film-on-water (FOW) test (Figure 4a) is a pseudo freestanding tensile test that can measure the mechanical properties of ultrathin films, including gold<sup>18</sup> and poly(3-hexylthiophene) (P3HT)<sup>9</sup>. The high surface tension of water (73 mN m<sup>-1</sup>) enables thin films to float on water surface and the low viscosity allows for nearly frictionless sliding of the thin films. After the film was transferred to the water surface, both ends of dog-bone

shaped films were attached to PDMS-coated manipulators fixed on the linear stage (Figure 4b). The attachment of COF films on PDMS was through Van der Waals adhesive forces, and no external mechanical fastening or adhesive bonding was needed.<sup>18</sup> We found that only films with appropriate thickness could be attached to the PDMS firmly. Thin films suffer from fracture at the edges, while thick films could not be attached through Van der Waals' adhesive force. Therefore, we selected COF films with the thickness of approximately 90 nm prepared using 24 mg mL<sup>-1</sup> concentration. One end of the manipulators was connected to the moving stage, and the other end was connected to a load cell (Kyowa, LTS 50GA). Both the moving stage and load cell were calibrated to measure the displacement and the stress of the film. Then, the film was stretched at a strain rate of  $0.3 \times 10^{-3}$  per second through the syringe pump until the film fractured (Figure 4c). The stress-strain curve data was obtained using the load cell and the associated software (MM01 MultiDAQ). The test was repeated three times to ensure the accuracy and to reduce random errors. The detailed setup is shown in Figure S16.

Stress-strain curves for the tested COF films are shown in Figure 4d and Figure S17. We calculated a crack onset strain of  $2.57 \pm 0.06$  % and Young's modulus of  $1.45 \pm 0.04$  GPa (Figure 4e). The Young's modulus was over five-fold larger than that for P3HT (approx. 0.26 GPa) as measured by the FOW test.<sup>9</sup> The modulus of the COF film was much higher than other soft materials including PDMS, rubbers, and most commercial polymers (see Figure 4f).<sup>23</sup> While the modulus we measured was lower than that for MOFs<sup>24–28</sup> and for highly crystalline polymers, such as poly(p-phenylene terephthalamide),<sup>29</sup> the modulus was the same order of magnitude as that of polyCOFs reported by Zhang *et al.*<sup>30</sup>

## CONCLUSIONS

In conclusion, we prepared, patterned, and transferred COF thin films to the surface of water for direct tensile testing. This patterning strategy will be useful for other applications, such as thin film electronics where patterning is important. Also, our approach to film transfer offers a straightforward method to produce free-standing COF films. Furthermore, the film-onwater tensile test provides a simple, generally applicable approach to characterize the mechanical properties of nanoscale COF films and advances the development of COF films for electronics, membranes, separators, and other applications where robust mechanical properties are important.

## EXPERIMENTAL SECTION

Synthesis of TAPB-PDA COF powders. TAPB (~21 mg, 0.06mmol) and PDA (~12 mg, 0.09 mmol) were weighed and dissolved in a mixture of 1.6 mL dioxane and 0.4 mL mesitylene in a Pyrex tube. The tube was sonicated until all powders dissolved. Then 0.2 mL 6M acetic acid was added and the solution was sonicated for 10 minutes. The tube was degassed three times through freeze–pump–thaw technique, then evacuated to an internal pressure of 150 mTorr, and flame-sealed. The sealed tubes were warmed to room temperature and transferred into oven and heated at 120 °C for 3 days. Yellowish powders precipitated out and were separated and washed thoroughly using THF and ethanol. Next, the wet samples were loaded in a tea bag and dried through supercritical  $CO_2$  technique in the Leica EM CPD300 Critical Point Dryer using an auto mode.

Characterization. PXRD data were recorded on a Rigaku SmartLab XRD from  $2\theta = 1^{\circ}$  up to  $30^{\circ}$  with  $0.02^{\circ}$  increment. COF samples were leveled flat on zero background sample holders. Fourier-transform infrared spectroscopy (FTIR) of all solid samples were tested using a ThermoNicolet iS10 FTIR spectrometer with a diamond ATR attachment and are uncorrected. Nitrogen sorption measurements were conducted on Quantachrome Autosorb-iQ-MP/Kr BET Surface Analyzer. Samples after ScCO<sub>2</sub> drying were degassed at 120 °C to remove any possible residue CO<sub>2</sub> molecules and tested immediately. BET surface areas were determined using BET adsorption models included in the instrument software (ASiOwin version 5.2). Scanning electron microscopy (SEM) was performed on a FEI Quanta 400 FESEM operating at 30.00 kV. Samples were prepared by dispersing COF powders in ethanol and dropping on clean aluminum sample holders. After drying for 24 hours, samples were coated with a 10 nm gold using a Denton Desk V Sputter. Transmission electron microscopy (TEM) of COF powders was performed using a JEOL 2100 Field Emission Gun Transmission Electron Microscope operating at 300 keV equipped with a Gatan (Gatan, Inc., Pleasanton, CA) One View-IS camera (FEG Emission: 15 µA, spot size 5, 150 µm CL aperture, exposure time of 0.5 s). All image acquisition was done using the Gatan Microscopy Suite (GMS), Digital Micrograph (Gatan, Inc., Pleasanton, CA). Atomic-force microscopy (AFM) images were obtained with ScanAsyst tapping mode using Bruker Multimode 8 microscope. Samples were prepared by scratching COF films using scotch tape. AFM tip was placed around the edge of film and thus the height information was recorded. Grazing-incidence wide-angle X-ray scattering (GIWAXS) data were collected at Sector 8-ID-E of the Advanced Photon Source at Argonne National Laboratory. The beam energy is 11 keV and the incident angle is around 0.13°.

**Static contact angle measurements.** Static contact angle measurements were carried out with a Krüss Instruments Drop Shape Analyzer DSA 100 at ambient conditions. Deionized water was used as testing liquids. Contact angles were measured 30 s after contact with testing. The reported contact angles reflected average values with standard deviation from at least three measurements from different regions of each sample.

**Dissolution of COF powders**. TAPB-PDA COF (24 mg) was weighed in a vial followed by addition of pure TFA (1 mL) and deionized water (deionized water,  $50 \,\mu$ L). After addition of TFA, the yellow powders became reddish immediately. Next, the solution was sonicated for a while until all powders dissolved and a red clear solution was obtained.

**Spin coating.** Microscope glass slide was first cut into 2.5 cm  $\times$  2.5 cm size, washed using soapy water, deionized water, acetone and isopropanol to remove any contaminants on the surface, and dried in oven at 100 °C for 1 hour. Next, the glass slides were further cleaved and treated using UV-ozone for 30 minutes to make the surface more hydrophilic.

**Preparation of PDMS cover.** PDMS was prepared by mixing silicone elastomer base with curing agent at 10:1 weight percent ratio in a glass petri dish and was then cured at 90 °C for 3 h. After cooling down, PDMS was peeled off and cut into a dog-bone shaped cover (dimensional size is given in Figure S12).

Sample preparation and film transfer for tensile testing. As-prepared solution (100  $\mu$ L) was dropped at the center of the glass slide using a pipette, and then it was spin coated at a speed of 2000 rpm to obtain a homogeneous film. Two dog-bone shaped PDMS covers were attached closely on the surface of film without any void. The glass slides were placed in the oxygen plasma cleaner for 20 minutes. COF films without PDMS cover were etched by the corrosive oxygen plasma, while those parts covered by PDMS remain on the glass slide. Next, PDMS covers were removed very carefully (see Figure S18) and the obtained dog-bone shaped COF films were deprotonated and activated thoroughly by being immersed in triethylamine and methanol. The deprotonated COF films were peeled off very carefully by immersing the glass slide aslant in water. High surface tension of water facilitated the peel-off of COF films.

# ASSOCIATED CONTENT

Supporting Information. Materials and methods, additional experimental details including photographs of experimental setup, and additional characterization data.

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