

Polycrystalline Covalent Organic Frameworks: Multiscale Structural Insights from Morphological Diversity to Dynamic Lattice Evolution

Juan Li[‡], Yukun Liu[‡], Xuezheng Tian[¶], Shulin Chen[‡], Shanshan Tao[¶], Masaki Takeguchi[§], and Donglin Jiang^{¶*}

[‡]*Institute of Crystalline Materials, Shanxi University, Taiyuan 03006, China*

[¶]*School of Physics, Sun Yat-sen University, Guangzhou 510275, China*

[†]*Changsha Semiconductor Technology and Application Innovation Research Institute, College of Semiconductors (College of Integrated Circuits), Hunan University, Changsha 410082, China*

[§]*National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan*

[¶]*Department of Chemistry, Faculty of Science, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore*

ABSTRACT: Covalent organic frameworks are a class of crystalline porous materials with covalent skeletons and inherent pores. They are prepared through a topology-directed polymerization process and usually obtained as polycrystalline materials. Despite rapid progress in materials synthesis and functional expansion, less is known about the structures of polycrystalline frameworks. This situation is ubiquitous in most cases, which complicate comparisons between frameworks, preclude the finding of intrinsic properties, and impede discrete structure-property correlations. In this work, we report structures of polycrystalline frameworks, by uncovering the coexistence of different morphologies and their static and dynamic behaviors, disclosing a realistic picture and multiple scale insights into structures of the most frequently used polycrystalline frameworks. Visualization with high resolution transmission electron microscopy revealed four distinct morphologies, i.e. nanoparticle aggregates, nanorod aggregates, ultrathin nanosheets, and parasitic fusion entities. Moreover, direct visualization revealed the existence of different polygons and channels and their contents, together with their boundaries and unstructured complements. Our studies revealed new assembly mechanisms via covalent-bond-mediated nanoparticle fusion and amorphous-phase-interconnected crystalline domain formation, providing foundation for synthesizing high quality crystalline porous frameworks and exploring their potentials of properties and functions.

Introduction

Covalent organic frameworks (COFs) present a fascinating class of crystalline porous materials by integrating organic units through covalent bonds to form crystalline skeletons and inherent pores.¹⁻⁴ COFs are prepared through polymerization via a topology-diagram-directed growth process, which relies on the precise geometry matching between monomers to guide the growth directions of covalent linkages and thus the lattices. They are usually obtained as polycrystalline materials, which have been widely used to develop different properties and functions.⁵⁻¹⁶ COFs are often characterized by powder X-ray diffraction (PXRD) to predict assumed crystal structures, while their real structures remain largely unclear. Although infrared spectroscopy, nuclear magnetic resonance spectroscopy, elemental analysis along with X-ray photoelectron spectroscopy can identify the covalent bond formation, how these linkages exist in the lattices are unclear.¹⁷⁻²⁶ These situations pose a long lasting yet common issue that polycrystalline COFs are unclear both in micro and

macro structures. This intrigues a big curiosity in elucidating the structure nature of polycrystalline COFs.

Despite rapid progress in materials synthesis and functional expansion over the past two decades, the uncertainty of polycrystalline COFs in term of structures causes general concerns about their inherent properties and clear structure-property correlations.^{27, 28} In this study, we focused on polycrystalline COFs by showing their structural evolutions at different scales. Direct visualization with transmission electron microscopy (TEM) enables us to observe the coexistence of different morphologies and dynamic lattices, which disclose a realistic picture of structures of the most frequently used crystalline porous COFs. We find that at macro levels, polycrystalline COFs consist of four morphologies, *i. e.* nanoparticle aggregates (NPAs), nanorod aggregates (NRAs), ultrathin nanosheets (NSs), and parasitic fusion entities (PFEs). More importantly, TEM visualization interconnected crystalline domain formation, underpinning the synthesis of high quality crystalline porous frameworks and the development of their inherent properties and functions.

Results and Discussion

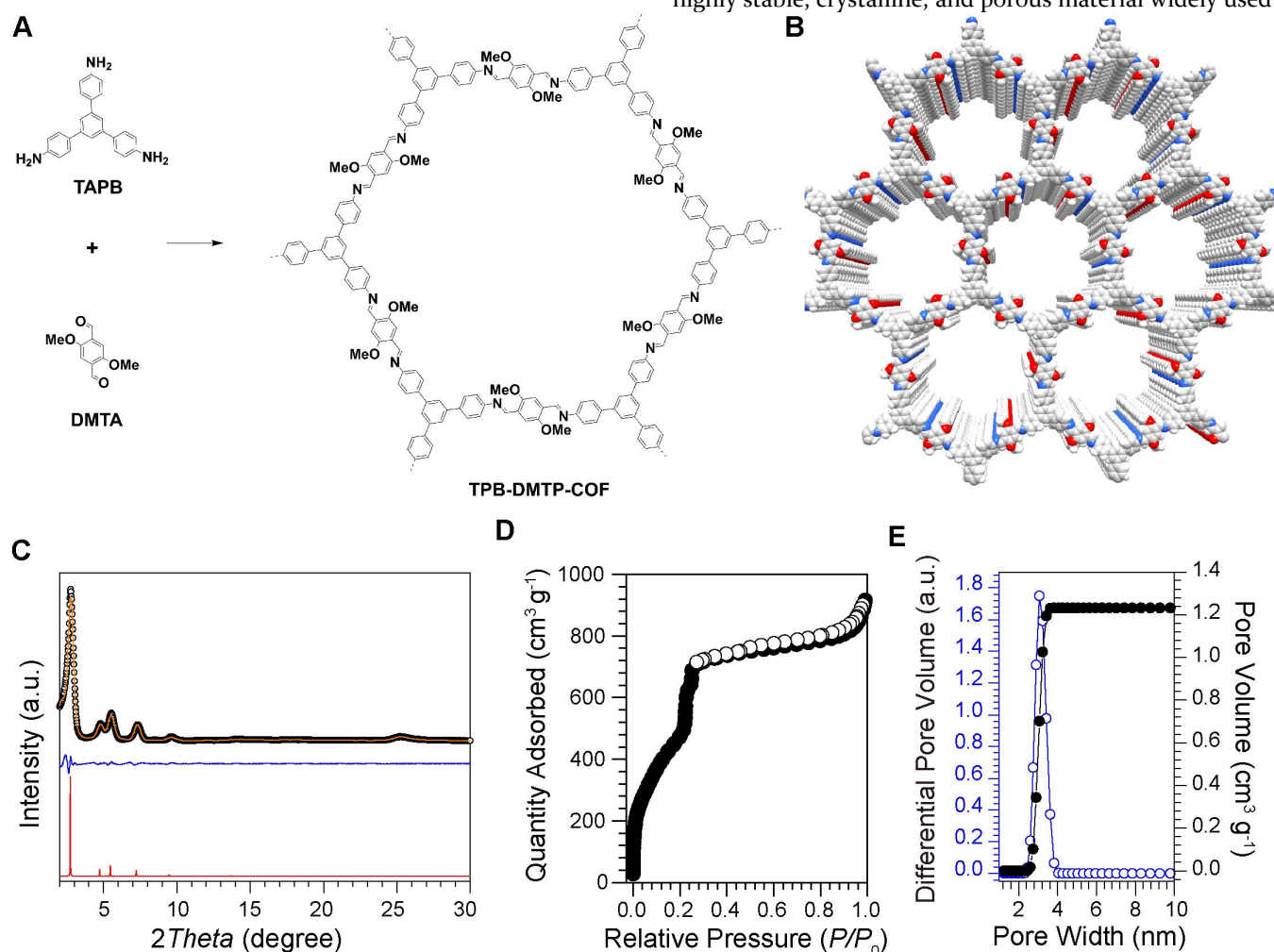


Figure 1. Crystal and Chemical Structures. (A) Synthetic scheme of TPB-DMTP-COF. (B) Reconstructed crystal structure. (C) PXRD pattern of TPB-DMTP-COF (black circles), the Pawley refinement result (orange curve) and their difference (blue curve), the AA-stacking mode of the P_6 space group (red curve). (D) N_2 adsorption isotherm curves. (E) Pore size (blue dot) and pore size distribution (black dots) profiles of TPB-DMTP-COF.

as a benchmark for exploring diverse properties and functions, from catalysis to ion conduction and membrane separation.^{14, 29, 31-35.}

Synthesis. We synthesized TPB-DMTP-COF (Figure 1A) by condensing 1,3,5-tris(4-aminophenyl)benzene (TAPB, 28.1 mg) and 2,5-dimethoxyterephthalaldehyde (DMTA, 23.3 mg) in a mixture of *o*-dichlorobenzene (*o*-DCB, 0.5 mL) and *n*-butanol (*n*-BuOH, 0.5 mL) at a 1/1 volumetric ratio with acetic acid (6 M, 0.1 mL) as catalyst in ampule (10 mL) at 120 °C for three days, followed by Soxhlet washing with tetrahydrofuran (THF) and dried under vacuum (Figure 1A). Through this process, polycrystalline TPB-DMTP-COF was synthesized in a yield of 90% (Figure 1B).^{29,30} PXRD revealed that TPB-DMTP-COF exhibited prominent peaks at 2.76°, 4.82°, 5.60°, 7.42°, 9.70°, 14.08°, and 25.2°, which were assigned to the 100, 110, 200, 210, 220, 500 and 001 facets, respectively (Figure 1C), which is similar to those synthesized with other solvents and reported ones.^{29,30} TPB-DMTP-COF adopts a space group of P_6 , with unit-cell parameters of $a=b=37.2718$ Å,

$c=3.5215$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. This space group and corresponding lattice parameters resulted in a simulated PXRD pattern (Figure 1C, orange curve) that was consistent with the experimentally observed curve. Pawley refinement (Figure 1C, red curve) also confirmed the assignment of the PXRD peaks, as evidenced by the negligible difference (Figure 1C, blue curve). Figure 1B shows the stacking structure. Nitrogen sorption isotherm analysis revealed that the Brunauer-Emmett-Teller (BET) surface area and pore volume are 1852 cm² g⁻¹ (Figure 1D) and 1.23 cm³ g⁻¹ (Figure 1E, black dot), respectively. By using the non-local density-functional theory (NLDFT) model, the pore size distribution analysis shows that the average pore size is 3.1 nm (Figure 1E, blue dot), which is consistent with TPB-DMTP-COF so far reported.³⁰

Screening of Dispersion Conditions. To obtain thin specimens suitable for TEM imaging, we investigated various dispersion parameters, including the solvent selection, ultrasonication conditions, centrifugation protocols, and grid type. We selected five high surface

tension organic solvents as dispersants: *N*-methyl pyrrolidone (NMP; 40.7 mN m⁻¹), Dimethylacetamide (DMAc; 36.4 mN m⁻¹), isopropyl alcohol (IPA, 22.7 mN m⁻¹), tetrahydrofuran (THF, 26.4 mN m⁻¹), and *n*-Butanol (24.6 mN m⁻¹), commonly used for exfoliating 2D materials including graphene.³⁶⁻⁴⁸ Water has a high surface tension of 72.8 mN m⁻¹ and features a small molecular volume. TPB-DMTP-COF is hydrophobic yet stable in water,^{30, 49} we thus included water as a solvent for the exfoliation of TPB-DMTP-COF.⁴⁷ We set the concentration of TPB-DMTP-COF at 0.25 mg mL⁻¹.

Probe-tip sonication (300 W, 10% output) demonstrated markedly superior exfoliation efficiency compared to bath sonication, as quantified by UV-vis absorbance measurements (Figures S1, S2, S5-S8) and particle size distribution analysis (Figure S3, S4).^{40,48} This enhancement arises from the localized energy transfer and direct cavitation effects inherent to probe ultrasonication, which effectively disrupts the strong interlayer π - π interactions and van der Waals forces in COF aggregates. To minimize potential structural degradation from prolonged ultrasonic exposure, pulsed operation cycles (2s on/2s off) coupled with active ice-bath cooling were implemented throughout the 30-minute processing window. Extended sonication durations (> 30 min) were empirically determined to induce no further exfoliation benefits while risking lattice defects.

Post-sonication, centrifugal separation parameters were optimized using Stokes' law formalism:

$$V = \frac{r \cdot (2\pi N/60)^2}{g} \cdot \frac{(\rho_s - \rho)d^2}{18\mu}$$

, which correlates sedimentation velocity (V , cm s⁻¹) with particle density (ρ_s , g cm⁻³), solvent density (ρ , g cm⁻³), medium viscosity (μ , g cm⁻¹ s⁻¹), particle diameter (d , cm), centrifugal rotation speed (N , rpm) and the radius (r , cm). A rotational speed of 1000 rpm was selected based on established protocols for carbon nanomaterials^{36, 39, 40, 43-48}, balancing supernatant retention of submicron particles with gentle separation dynamics. The separation time (T) was rationalized and optimized through computational modeling based on the following expression (see Supporting Information):

$$T = \frac{(\ln r_{\max} - \ln r_{\min})/3600 \cdot (2\pi N/60)^2}{(\rho_s - \rho) \cdot d^2/18\mu}$$

To obtain ideal COF specimens with optimal thickness for TEM observations, a controlled sedimentation strategy was implemented. Theoretical calculations assumed $\rho_s - \rho = 0.5$ g cm⁻³ and a particle size cutoff of 1 μ m, requiring a minimum sedimentation time of 50 minutes. We settled the sedimentation time for 1 hour to enable effective gravitational separation of thicker agglomerates while retaining ultrathin nanosheets in suspension. This time-optimized sedimentation process effectively removes denser particulate matter through centrifugal sedimentation, thereby ensuring that the remaining colloidal dispersion contains predominantly well-dispersed COFs suitable for high-resolution TEM imaging.

Using a weight-based calculation, the exfoliation efficiencies in NMP, DMAc, IPA, THF, *n*-BuOH, and water were 52%, 40%, 36%, 36%, 36%, and 36%, respectively (Table S1). This result indicates that NMP serves as the optimal solvent. Prolonging ultrasonication time did not increase dispersion efficiency (Figures S6-S8), suggesting that the exfoliation efficiency is controlled by the polarity and surface energy of solvent. A hanging method was used to deposit a drop of the supernatant onto the grid, left undisturbed to air-dry naturally. The grid was then transferred into a drying cabinet for 12 hours before TEM observation. The selection of an appropriate grid proved crucial for high-resolution imaging of COF lattice fringes. Through systematic comparison of ultra-thin carbon films, microgrids, and conventional holey carbon films, we identified that the use of a Quantifoil® support film (400 mesh) with well-defined, uniformly distributed holes enabled the successful acquisition of microstructure morphology of COFs in our characterization studies.

Morphology Diversity. In the initial step, a biological transmission electron microscope (Hitachi-7650) was employed to observe the TPB-DMTP-COF sample, with an accelerating voltage of 100 kV. Through a meticulous check for thousands of images, we confirmed four distinct types of morphology within TPB-DMTP-COF, i.e. NPAs, NRAs, NSs, and PFEs.

The first type of morphology is in the form of NPAs, as clearly shown in Figure 2A. This aggregation structure is characterized by a cluster morphology, which emerges from the cohesive interaction among nanoparticles of relatively uniform dimensions. These nanoparticles are 30–50 nm in size and assemble into clusters through robust covalent crosslinking. Moreover, these nanoparticles display a hexagonal form, which significantly enhances the unique and recognizable morphological features of the aggregates. This NPA structure resembles the oriented attachment mechanism observed in inorganic nanocrystals.⁵⁰⁻⁵⁸

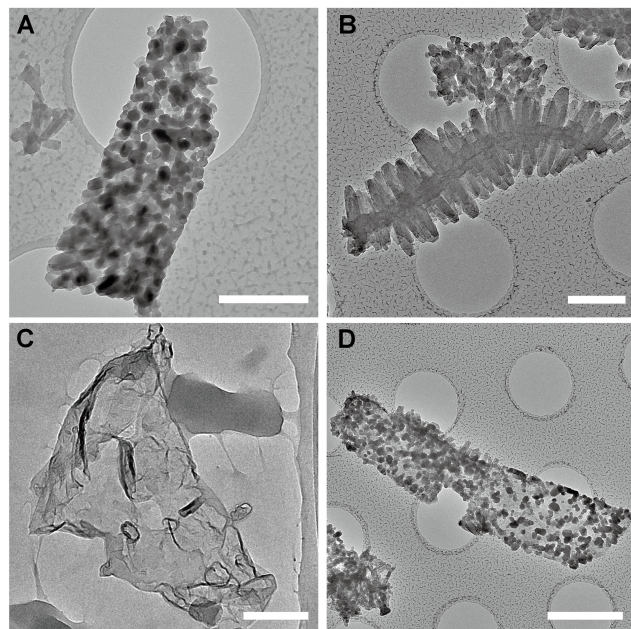


Figure 2. Diversity of the morphology of polycrystalline TPB-DMTP-COF. (A) NPs, (B) NRAs, (C) NSs, (D) PFEs. Scale bars: 500 nm (A, B), 200 nm (C), 1 μ m (D).

TPB-DMTP-COF presents another morphology – NRAs, which distinguished from the first one on nanoparticles, featuring nanorod as the elementary unit (Figure 2B). NRAs are arranged in such a way that the entire cluster exhibits a striking radial pattern, with a width of approximately 30 to 50 nm and a length extending to around 1 μ m.

Interestingly, both NPs and NRAs exhibited remarkable stability, to the extent that they could not be dispersed into discrete particles even upon alkali treatment and multi-cycle exfoliation (Figures S9 – S12). This result indicates that these nanoparticles or nanorods in NPs and NRAs are connected by chemical bonds other than weak Van der Waals forces. These structural irregularities may contribute to the material's overall property, functionality, and performance, uncovering a hidden point that warrants further investigation.

The third morphology is distinguished by ultrathin nanosheets (NSs), closely resembling the morphology of two-dimensional (2D) materials (Figure 2C).

The fourth morphology – PFEs, represent a hierarchically structured nanocomposite, wherein 2D NSs and zero-dimensional (0D) nanoparticles are interpenetrated through interfacial coupling interactions, forming a mechanically robust architecture. This unique aggregate, resulting from the integration of these two distinct components, is termed PFEs (Figure 2D). This name aptly describes how the particles adhere to and interact with the nanosheets, creating a cohesive yet distinct entity.

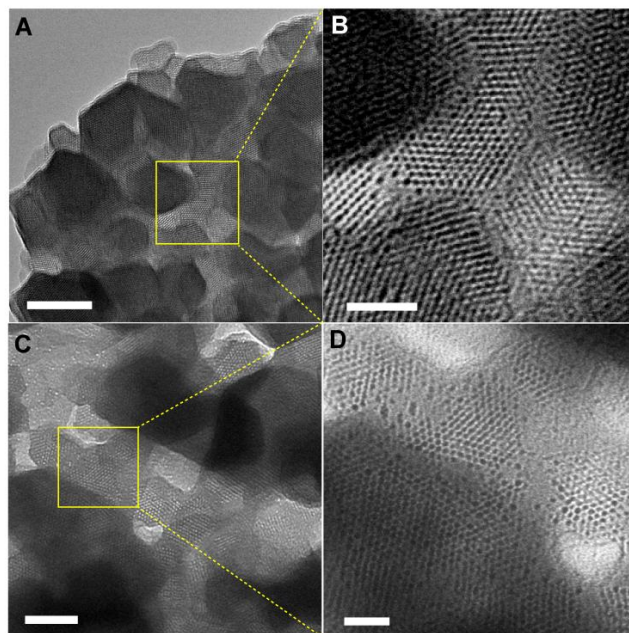


Figure 3. Micromorphology Structures of NPAs. (A and B) The TEM image (A) and its enlarged image (B) of selected region in (A). (C and D) The TEM image (C) and its enlarged image (D) of selected region in (C). Scale bars: 100 nm (A, C); 20 nm (B, D).

Micromorphological Structures of NPAs. As the most effective dispersant, NMP enabled clearer observation of micromorphologies of NPAs. As shown in Figure 3A, the boundary between the crystalline domains in NPAs was remarkably discernible. Owing to variations in crystal orientation from one particle to another, grain boundaries emerge because of the non-directional contact between them. Additionally, a detailed examination of Figure 3D revealed that the porous structure is not composed solely of regular hexagons, instead, a large number of deformed hexagons are ubiquitous.

In the enlarged TEM image as shown in Figure 3B, TPB-DMTP-COF exhibited a striking tree-branch structure as it propagates along the z-axis. Moreover, the crystalline domains do not directly contact with one another. Instead, they are interconnected by an amorphous phase (Figure 3C, 3D). This mode of interconnection likely endows COFs with inherent rubber-like elasticity and toughness. Such structures are supposed to be highly advantageous for applications that demand flexible and resilient porous materials, potentially opening new avenues for the utilization of COFs in various industries.

Micromorphological Structures of NRAs. The nanostructures of NRAs were systematically investigated (Figure 4). In NRAs, the pore structure appears in a striped configuration, which is due to the "lying" orientation of the nanorods. Notably, NRAs were not distinctly segregated from NPs but rather exhibited an intergrown architecture. This observation suggests two possible growth pathways: either NRA represent an advanced growth stage of NPA, or they originate from interconnected single COF particles that expose specific

crystal facets and subsequently undergo uniaxial growth, forming characteristic "exploded head" morphologies. Figure 4B presents a magnified view of the selected area marked in Figure 4A, revealing that the COF nanorods maintain a consistent width (~ 30 nm), matching the dimension of nanocrystal, while their lengths extend to several micrometers. This significant aspect ratio highlights the anisotropic growth behavior of COF nanocrystals, demonstrating pronounced preferential orientation during crystallization.

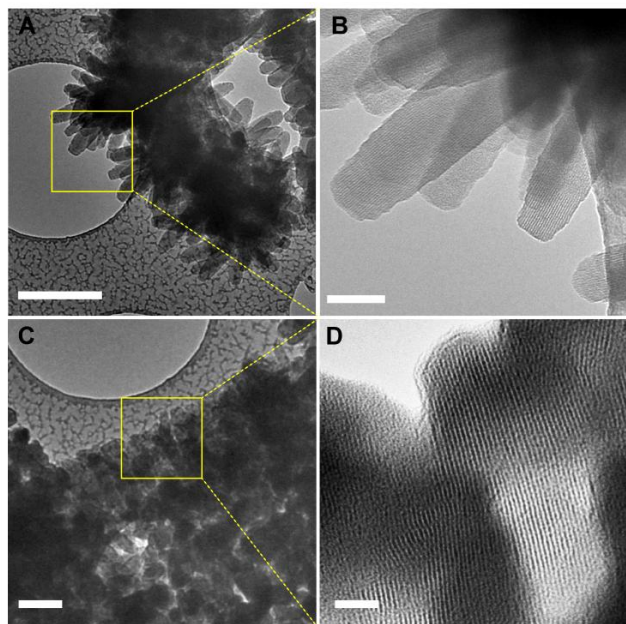


Figure 4. Micromorphology Structures of COF NRs. (A and B) The TEM image (A) and its enlarged image (B) of selected region in (A). (C and D) The TEM image (C) and its enlarged image (D) of selected region in (C). Scale bars: 500 nm (A), 50 nm (B), 500 nm (C), 20 nm (D).

Further structural evolution was captured in Figure 4D (a magnified region of Figure 4C), which revealed remarkable branching phenomena during nanocrystal growth. Close examination of the branching nodes shows distinct lattice constriction at the bifurcation points, a phenomenon we attribute to the cis-trans isomerization of imine linkages and associated bond cleavage events.^{59, 27} Additionally, bending features observed in COF nanorods (Figure S13) can be rationalized through this branching mechanism, where asymmetrical growth at bifurcation points induces curvature in the nanostructures. These structural modifications provide critical insights into the dynamic reorganization of COFs during crystallization processes.

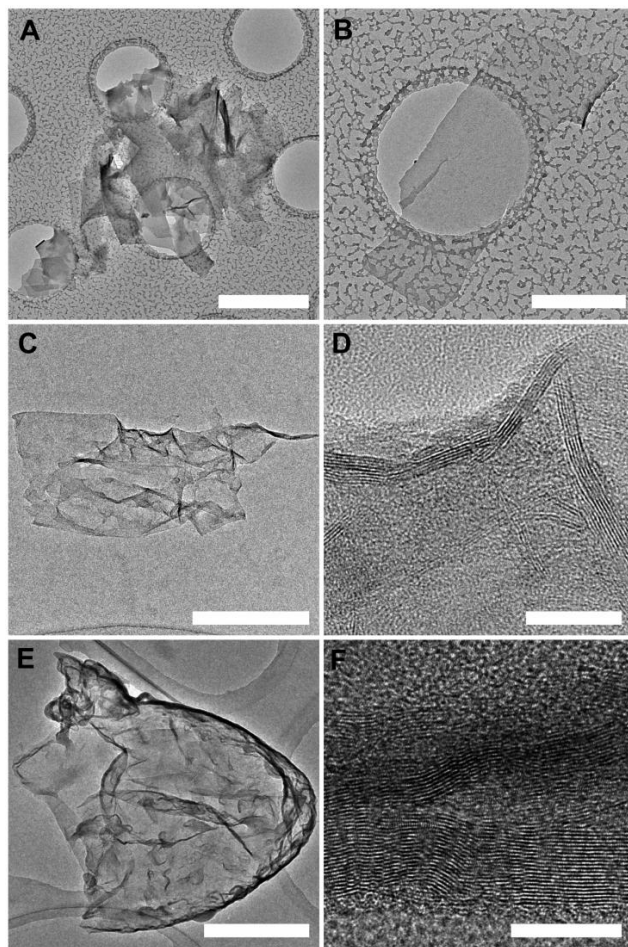


Figure 5. TEM Images. (A–F) TEM images of NSs. (D) Enlarged image of the folded edge of selected region in (C). (F) Enlarged image of the folded edge of selected region in (E). Scale bars: μm (A), 500 nm (B, E), 200 nm (C), 10 nm (D, F).

Micromorphological Structures of NSs. In an ideal scenario, 2D COFs would adopt a well-defined nanosheet morphology analogous to classical 2D materials such as graphene, provided they are formed according to the idealized reaction scheme. While NPAs and NRAs have been established as the primary structural determinants of COF architectures, detailed characterization of nanosheet structures remains imperative due to their relevance to film and membrane – a pivotal requirement for industrial implementation.

The successful isolation of nanosheets from disordered bulk COF systems was achieved through systematic optimization of delamination parameters based on our established dispersion protocol (Figure 5A–F). Cross-sectional analysis (Figure 5D) confirmed that the separated NSs exhibit thicknesses of several nanometers. Notably, despite reaching this theoretically optimal thickness for structural characterization, the characteristic (110) plane diffraction signature remained undetectable regardless of detection methodology – a finding consistent across both Hitachi 7650 and JEM-ARM-200F. Intriguingly, high-resolution imaging revealed

well-defined stratified stacking structures corresponding to the (001) planes at folded NS edges, displaying an interlayer spacing of 3.4 Å that matches precisely with PXRD results.^{29, 30, 33-35, 49} The layer architecture exhibited discontinuous (Figure 5D), branched configurations (Figure 5F) with distinct terracing features, indicative of significant interlayer dislocations and localized amorphous domains within the NS framework. Comprehensive morphological analysis of multiple NS regions further revealed heterogeneous electron contrast patterns and structural discontinuities (Figure S14), indicative of substantial thickness variations within individual NSs.

Micromorphological Structures of PFEs. The structural features of the fourth COF morphology, identified as PFE, are illustrated in Figure 6. Figure 6A demonstrates that PFEs comprise discrete COF nanocrystals intimately integrated with COF nanosheets. These observations, combined with our systematic morphological studies, elucidate critical aspects of COF interfacial phases between COF crystallites, where COF nanoparticles (NPs) interconnect through amorphous phases to form NSs with discontinuous crystalline domains (Figure 6B). This structural evolution supports our proposal that COF NSs derive from NPA ripening and

fusion, as consistently observed in our microscopic studies.

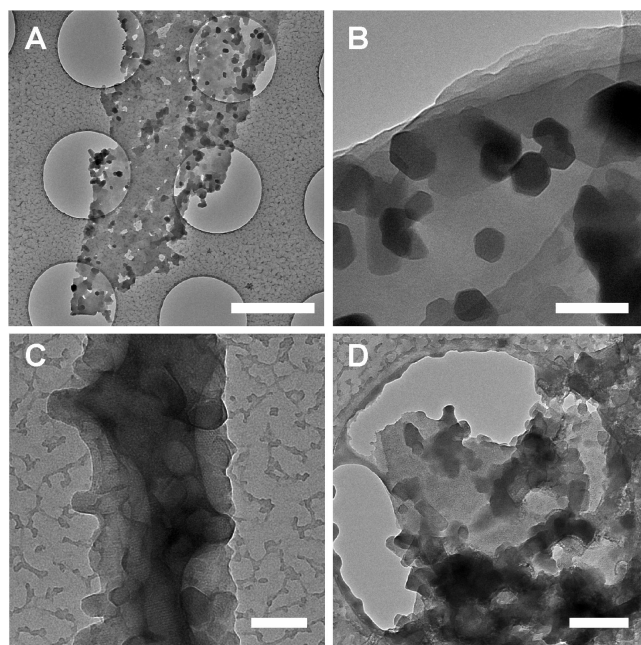


Figure 6. TEM Images. (A-D) TEM images of PFEs. Scale bars: 1 μm (A), 100 nm (B, C), 200 nm (D).

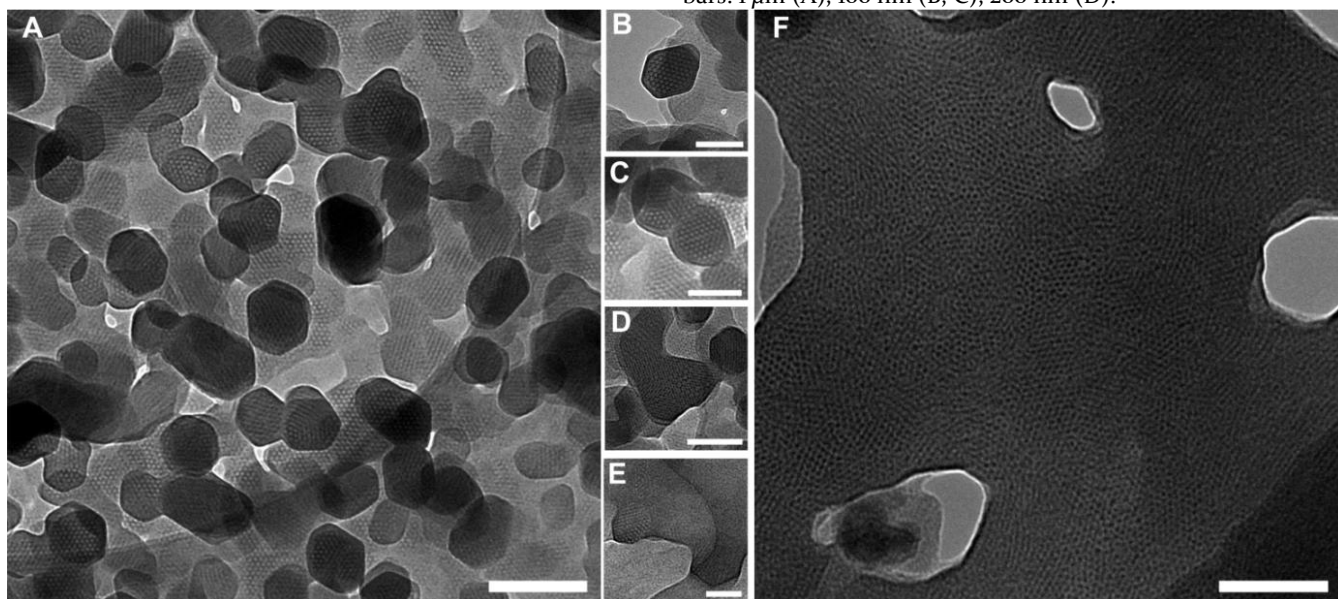


Figure 7. TEM images. (A) Low-magnification overview of the NPAs structure. (B-E) Higher-magnification images of an individual nanocrystal (B), twin nanocrystal (C), three nanocrystal (D), and fusion entity (E). (F) Low-magnification overview of the NSs structure. Scale bars: 100 nm (A), 50 nm (B-F).

Figure 6C displays a representative fused architecture retaining faceted NPs morphology at its edges, with distinct hexagonal lattice features. Collectively, these findings suggest NSs formation may occur through the NPAs maturation, where NPs progressively coalesce via elastic amorphous intermediates into consolidated architectures (Figure 6D). In PFEs, surface-distributed COF nanocrystals may represent either primary products from NPAs fusion or secondary growths nucleated preferentially at crystalline domain boundaries within the NSs matrix. This dual mechanism accounts for both

preserved NPs morphology and emergent structural order during NSs development.

We also surveyed sp^2 carbon-conjugated COFs with tetragonal topology and double-bond linkages, and isostructural COFs synthesized under different solvothermal conditions or with methyl substituted edge units (Figure S15-17). The four micro-morphologies were found to be universal in COF powders despite variations in topology, synthesis, and building units. While the proportions of these morphologies can be influenced by assembly units, covalent bond types, and synthesis

conditions, strong aggregation, non-exfoliability, and fusion growth are inherent morphological characteristics of COFs.

Pore Structures. Unexpectedly, despite water generally being considered less effective in terms of exfoliation efficiency, it enabled us easily to successfully capture the porous structure of TPB-DMTP-COF. In NPAs, a regular hexagonal porous architecture was observed, suggesting that the particles tend to exhibit a positive band axis structure (Figure 7A). Impressively, when water is used as the dispersion medium, the COF pore structures exhibit increased regularity, reduced structural deformation, and the resulting TPB-DMTP-COF particles more closely resemble single crystals. Figure 7B displayed the morphology of an individual COF nanoparticle, while Figure 7C revealed an intermediate state characterized by imperfect alignment between two distinct COF particles. Figure 7D demonstrates a perfectly oriented attachment configuration formed by three COF nanoparticles. The progressive fusion of nanoparticles into nanosheets is illustrated in Figure 7E, while Figure 7F presents the final nanosheet morphology, exhibiting discrete domains of discontinuously connected COF crystallites. These observations collectively suggest that the growth mechanism of COFs shares similarities with the oriented attachment mechanism observed in traditional inorganic nanocrystals.^{50-58, 60-67} However, distinct crystallization

features emerge due to the polymeric elasticity and covalent connectivity inherent to these organic frameworks, differentiating their crystallization pathway from conventional inorganic systems.

Notably, a striking deviation from conventional symmetry paradigms was observed in these COF particles. Contrary to the $P6$ or $P1$ symmetry configurations predicted by long-established lattice simulations (*e. g.* Material Studio software), the three (110) crystallographic planes of NPAs within the x - y plane exhibited significant anisotropic interplanar spacing heterogeneity. Profiles analysis of the selected regions in Figure 7B revealed detorted (100) lattice spacings along three orthogonal axes: $d_1 = 2.6$ nm, $d_2 = 2.9$ nm, and $d_3 = 2.6$ nm (Figure S18). This anisotropic behavior was verified through comparative measurements of NMP-dispersed TPB-DMTP-COF samples, where analogous characterization of the corresponding (100) planes yielded reduced spacings ($d_1' = 2.3$ nm, $d_2' = 2.5$ nm, $d_3' = 2.3$ nm) (Figure S19). The consistent observation of directional spacing variations across both dispersion systems confirms the inherent (100) plane anisotropy in COF architectures. The lattice contraction observed in NMP-dispersed specimens ($\Delta d = 0.4$ nm relative to aqueous-dispersed counterparts) is attributed to solvent-induced structural dilation, where NMP molecules likely induce lattice contraction

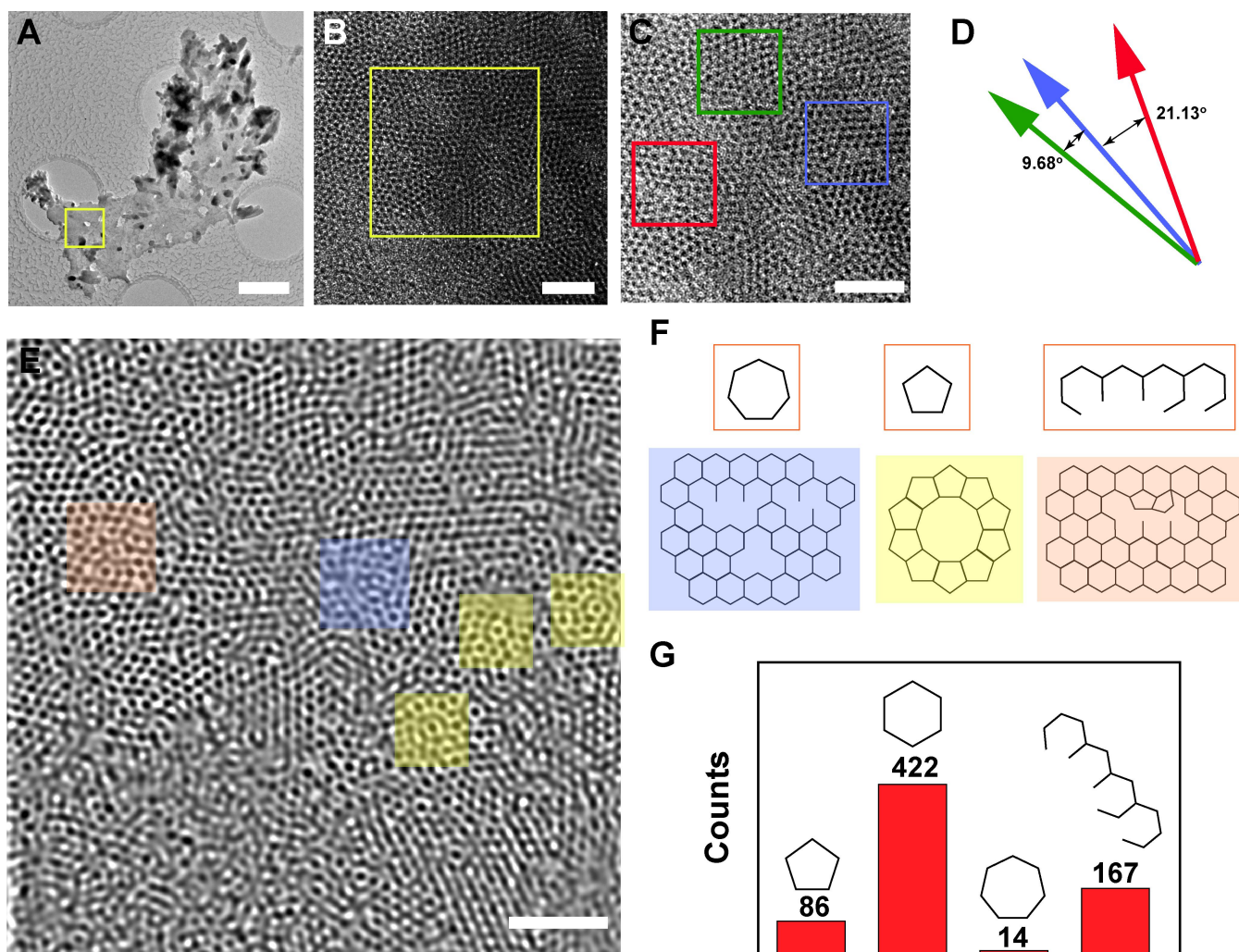


Figure 8. TEM Images. (A) Full-view image of a COF NS. (B) High magnification image of the selected area in (A) (yellow box). (C) Three consecutive regions in the designated area for analyzing angular relationships among crystal domains. (D) Schematic of the angles between crystalline domains in (C). (E) Bandpass filtered image of (B) to enhance clarity of the porous structure. (F) Schematic of three types of defect structures and their interconnections. (G) Statistical results of defect type counting in (E). Scale bars: 500 nm (A); 20 nm (B, C, E).

through tight interactions with the pore wall of TPB-DMTP-COF. The observed variations in lattice spacing may correlate with the compromised reproducibility of porous properties in COF materials over the past two decades.^{68, 69}

Morphological Details of NSs. As supported by the clear pore results, we used the water-exfoliated TPB-DMTP-COF to achieve atomic-level resolution by carrying out TEM on a Cs-corrected JEM-ARM200F-B equipped with a cold field emission gun (FEG). The microscopes were operated at a voltage of 80 kV, a setting designed to avoid or minimize the electron knock-on effects. We found that the NPAs was rather challenging to discern under this condition (Figure S20). Luckily, the porous structures in NSs were clearly visualized, as illustrated in Figure 8. Consistent with Figure 7F, the NSs were composed of a substantial number of crystalline domains, as evident by enlarging the area in Figure 8B. Clearly, each domain has an approximate size of 20 nm (Figure 8C). These domains were interconnected yet exhibited

different orientations. Specifically, three adjacent domain regions were selected, where the angles between them were measured to range from 9.68° to 21.13° (Figure 8D).

To improve the clarity of the pore structure within the NS, a bandpass filter was applied to the image of Figure 7B. This filtering process effectively eliminated the noise, resulting in the image depicted in Figure 8E. The NS revealed a multitude of continuous hexagonal lattices, accompanied by distinct defects. The main types of defects included pentagons, polygons formed by the connection of pentagons, and a significant number of channel-type structures arising from bond breaking (Figure 8F). Thus, we conducted a counting and statistical analysis on a selected area within the NS in Figure 8E. The counts of hexagons, pentagons, polygons, and channel structures are 422, 86, 14, and 167, respectively, revealing that 62.5% of defects in the COF nanosheets are the channel-type defect (Figure 8G). These results unambiguously suggest that extensive chemical bond

cleavage disrupts the long-range order of COFs, hindering their growth into large single crystals.

Low-Dose Electron Microscopy Imaging. Scanning transmission electron microscopy (STEM) modes have the advantage of avoiding the complex diffraction contrast and coherent imaging phenomena commonly observed in the HR-TEM images, enabling the generation of high-resolution, non-correlated images, hence we subsequently used a STEM mode (Nion Ultra-STEM 100) with an acceleration voltage of 60 kV to observe the polycrystalline TPB-DMTP-COF. To minimize the total electron dose, the images were captured using an electron beam current of 15 pA and a dwell time of 8 μ s per image, resulting in a total electron dose of 4.8 e⁻ Å⁻². Figure 9 depicted a representative annular dark field (ADF) image. NPAs are composed of stacked structures, with nanocrystals unevenly distributed (Figure 9A).

The sizes of these nanocrystals range from 20 nm to over a hundred nanometers. The lattice constants of COF specimen were directly measured (Figure 9C, D), which varied widely, ranging from 2.5 nm to 2.9 nm (Figure 9D), revealing significant distortion within the same COF particles. Consistent with the previous results, analysis of STEM electron microscope images indicates that the lattice spacing of TPB-DMTP-COF is not isotropic (Figure 9E). The structural characteristics of the COF NSs were further elucidated by STEM analysis. As illustrated in Figure 8F, the NSs exhibit a configuration comprised of discontinuous crystalline domains with lateral dimensions ranging from 20 to 50 nm, interconnected through an amorphous matrix.

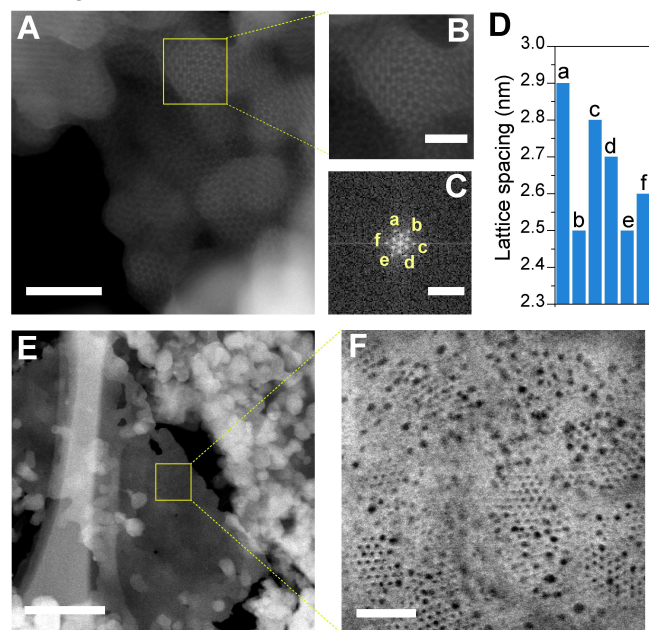


Figure 9. Structural Characterization of COFs via NION STEM. (A-C) Aberration-corrected STEM image of COF NS with insets: magnified view (B) of the selected area in A and corresponding FFT pattern (C). (D) Statistical distribution of lattice spacings from six diffraction spots in panel C. (E) Large-area morphology of NS. (F) Atomic-resolution

magnification of the yellow-boxed region in panel E. Scale bars: 50 nm (A), 20 nm (B, F), 1 nm (C), 500 nm (E).

Dynamic Lattice Evolution. As is evident from the foregoing discussion, in an attempt to mitigate the

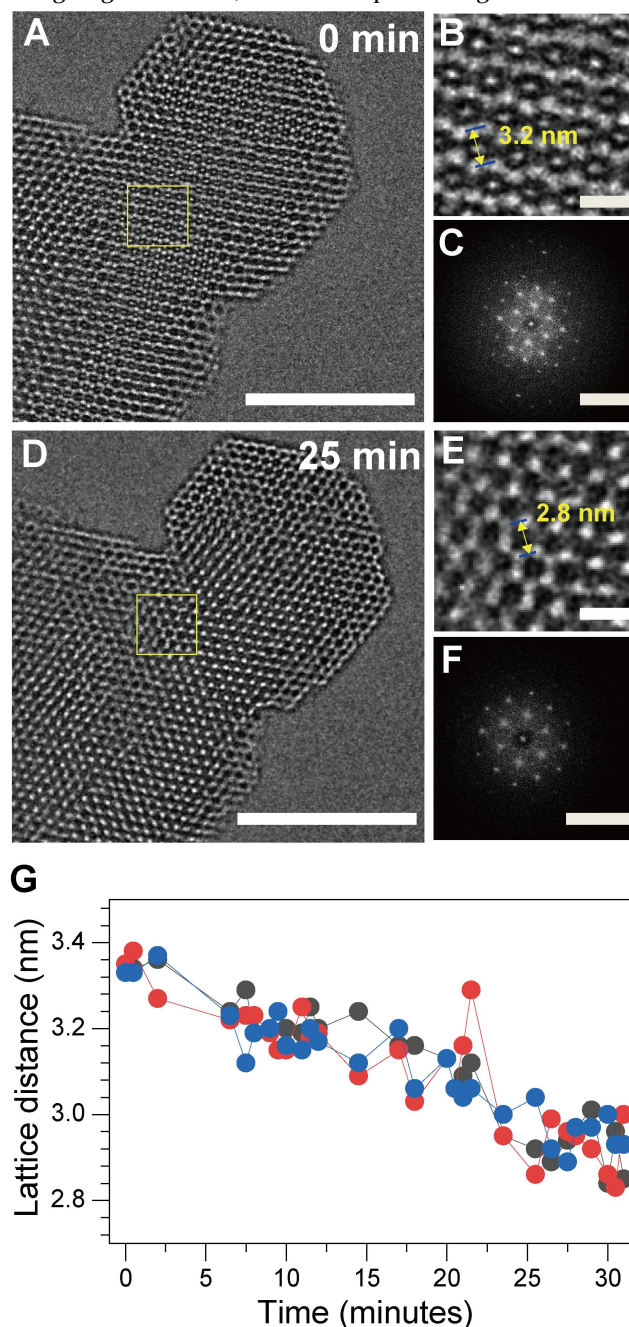


Figure 10. Time-Dependent Structural Evolution. (A) Initial HR TEM image of a twin-crystal of TPB-DMTP-COF dispersed by deionized H₂O (0 min; scale bar: 50 nm). (B) Enlarged view of the yellow-boxed region in (A) (Scale bar: 5 nm). (C) The FFT pattern of (A) (scale bar: 1 nm⁻¹). (D) The HR TEM image of the same specimen of (A) after 25 minutes (scale bar: 50 nm). (E) Enlarged view of the yellow-boxed region in (D) (Scale bar: 5 nm). (F) The FFT pattern of (D) (Scale bar: 1 nm⁻¹). (G) Quantitative analysis of (100) lattice spacing evolution over time.

structural damage inflicted upon COFs by the electron beam, our primary approach involved utilizing the low-

voltage mode. Nevertheless, a low acceleration voltage proves to be detrimental to the electron beam's penetration into the sample. This poses a significant obstacle to the acquisition of high-quality images of COFs. In recent years, the unceasing progress of electron beam acquisition technologies, such as the direct electron camera and integrated differential phase contrast (iDPC), coupled with sophisticated image alignment techniques,⁷⁰⁻⁷⁸ has substantially enhanced the imaging resolution for electron beam-sensitive materials. Building on the latest advancements in COFs electron microscopy characterization, direct detection electron microscopy (DDEC) combined with ultra-low dose imaging technology ($0.05 \text{ e}^- \text{ \AA}^{-2}$ per image) was employed at an acceleration voltage of 300 kV to further examine the microscopic morphology of TPB-DMTP-COF.

Given the ultrathin characteristics of water-dispersed COF samples that facilitate electron microscopy observation, the water-dispersed TPB-DMTP-COF was used for this investigation. Through optimized electron beam alignment and sample stabilization protocols, an unexpected discovery was made from a nearly perfect crystalline region where two nanocrystals were precisely aligned and perfectly oriented connected.

Real time monitoring of the sample's spatial configuration was implemented (Figure S21). During the observation period, a distinct high contrast feature emerged at the geometric center of the COF grain's nanopores, as shown in Figure 10A. This localized bright spot (Figure 10B, C) had relative contrast similar to the nodes of COFs (Figure S22), indicating a possible structural or compositional anomaly. The phenomenon's temporal evolution (Figure 10E) revealed a gradual reduction in the bright spot intensity (I/I_0) decreased from 1.0 to 0.3 over about 25 minutes (Figure 10C, Figure S23). Concurrently, the (100) interplanar spacing of TPB-DMTP-COF reduced from 3.2 nm to less than 2.8 nm ($\Delta d/d = 12.5\%$). This intriguing phenomenon sparks curiosity (Figure 10G). If the bright spot originates from reversible elastic slip of the COF stacking mode, it would be common rather than localized and would not disappear so readily.

This observation aligns rigorously with the high-resolution imaging results obtained in transmission mode, as previously discussed.

Given that the sample was prepared by dispersing it in deionized water, a hypothesis was formulated that the bright spot might represent a water cluster trapped within the COF pores, which had not been completely eliminated. To test this hypothesis, in-situ PXRD was used to monitor the diffraction behavior of TPB-DMTP-COF.

The COF powder was pressed into a compact pellet, saturated with water via a diffusion method, and then subjected to a heating dehydration experiment (Figure 11A-E). Compared to the completely dry sample, the hydrated TPB-DMTP-COF showed a significant shift and broadening of the (100) diffraction peaks, along with a

shoulder peak at 3.2° (Figure 11A). The diffraction peaks of the (110), (200), and (220) planes also exhibited remarkable broadening (Figure 11B). Notably, this lattice distortion persisted even when the temperature was raised to 453 K. Additionally, the COF powder's color changed from orange at 303 K to bright yellow as the temperature increased (Figures S24). Further vacuum drying (at 100 mbar) of the COF pellet revealed that lattice distortion still existed after 30 minutes

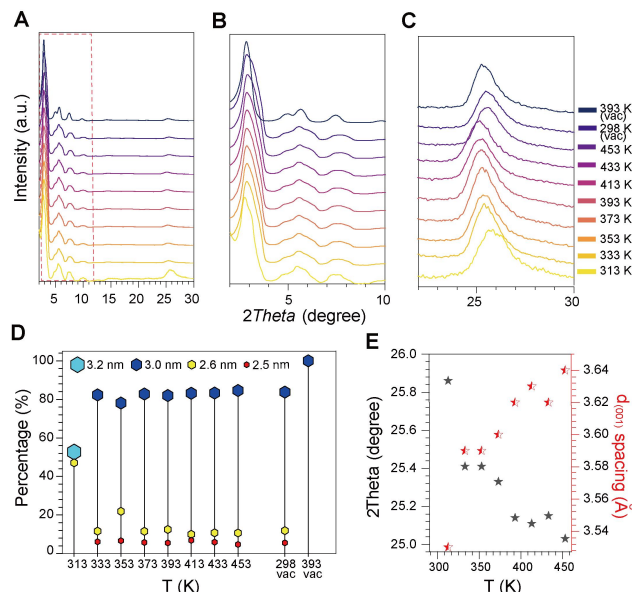


Figure 11. In situ PXRD Analysis upon Thermal Dehydration. (A) Temperature-dependent PXRD patterns (313 K - 453 K) showing structural evolution. (B) Magnified 2° - 10° region highlighting reversible (100) peak shifts. (C) Magnified 23° - 30° region highlighting reversible (001) peak shifts. (D) Grain size distribution from Scherrer analysis of (100) peaks, showing progressive size reduction. (E) Layer distance variation from Scherrer analysis of (001) peaks, showing progressive expansion.

of drying at 303 K. Only when the temperature was raised to 393 K and vacuum-dried for 30 minutes did the lattice distortion disappear completely.

Using Gaussian fitting to decompose the split (100) diffraction peaks, we found that the peak could be precisely divided into three distinct components (Figures S25-S35). Calculations using Bragg's equation indicated that, with water removal, a certain proportion of lattice-contracted COF particles emerged in the powder, with (100) lattice spacings of 3.0, 2.6, and 2.5 nm (Figure 11D, Table S2). Upon complete water removal, the smaller-lattice particles disappeared, and the lattice size reverted to a uniform 3.0 nm. Notably, although previous nitrogen adsorption combined with NLDFT simulation and crystal structure simulation suggested a pore size of 3.2 nm for TPB-DMTP-COF, the PXRD patterns indicated that the accurate diffraction peak corresponding to 3.2 nm was only obtained in the presence of certain moisture, indicating that moisture acts as a crystallization template for COFs to some extent.

The in-situ monitoring of the (001) diffraction peak for the hydrated TPB-DMTP-COF revealed a progressive shift toward lower angles with increasing temperature (Figure 11C), accompanied by an expansion of the interlayer spacing from 3.52 Å to 3.64 Å (Figure 11E). This observation demonstrates a distinct dynamic structural response during the thermally induced desorption of water molecules from the COF channels. Complementary in situ heating experiments on the pristine TPB-DMTP-COF showed no noticeable shift in the (100) diffraction peak, with the interlayer spacing remaining virtually unchanged (Figure S36). These comparative results unambiguously disclosed that the lattice distortion observed in the hydrated COF originates from the diffusive behavior of confined water molecules within the nanoporous architecture. Moreover, the contraction and expansion of the COF lattice as moisture diffuses out of the COF is consistent with the lattice contraction observed under low-dose techniques in this study, which motivates more in-depth exploration in future work.

CONCLUSION

In summary, we disclose a picture of structures of polycrystalline COFs, which are the most frequently used materials in the field. With advanced characterization techniques, we clarify key elements of structures and their dynamics. (1) Polycrystalline COFs consist of different morphologies of macro-objects, including nanoparticle aggregates, nanorod aggregates, nanosheets, and parasitic fusion entities. (2) These objects are in micrometer size, cannot be further exfoliated, and consist of covalently linked nanoparticles, nanorods, nanosheets, and nanoparticles with nanosheets, which have domain sizes of tens of nanometers. (3) The nanoparticles consist of tree-like crystalline domains which are interfaced by amorphous parts. (4) The COF nanorod aggregates can be considered as a stage-evolved product of nanoparticle aggregates growth, where solvent-COF nanocrystal interactions induce dynamic structural disruptions that compromise perfect $P6/P1$ symmetry. This crystallographic distortion generates anisotropic growth behavior in COF particles, promoting preferential development along specific crystallographic planes and ultimately leading to rod-shaped architectures through symmetry-broken crystallization. (5) The nanosheets consist of hexagonal pores, while holding various types of other polygons and channels, originating from defects of covalent bonds. (6) The nanosheets are formed by small crystalline domains of different orientations. (7) Parasitic fusion entities comprise discrete COF nanocrystals intimately integrated with COF nanosheets. (8) These objects feature covalent-bond-mediated nanoparticle or rod fusion and amorphous-phase-interconnected crystalline domain formation. (9) The single crystalline domains are dynamic and allow lattice expansion and reduction by guest molecules, demonstrating their rigid yet elastic nature.

Our results revealed general structural features of polycrystalline COFs from macro to micro scales in

conjunction with their interfaces and dynamics. These new insights deepen our understanding of COF materials and offer new guidance for achieving high quality COF materials.

ASSOCIATED CONTENT

Supporting Information.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

Experimental procedures and characterization data (PDF). Additional experimental details, materials, methods, including photographs of experimental setup, and characterization data (PDF). The deconvolution and fitting results and statistics of the PXRD diffraction patterns for COFs powders, and the crystal structure data of the COF.

AUTHOR INFORMATION

Corresponding Author

Donglin Jiang – Department of Chemistry, Faculty of Science, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore; <https://orcid.org/0000-0002-3785-1330>; Email: chmjd@nus.edu.sg

Authors

Juan Li – Institute of Crystalline Materials, Shanxi University, Taiyuan 03006, China; orcid.org/0000-0002-1557-3712

Yukun Liu – Institute of Crystalline Materials, Shanxi University, Taiyuan 03006, China; orcid.org/0000-0002-5604-3988

Xuezheng Tian – School of Physics, Sun Yat-sen University, Guangzhou 510275, China; orcid.org/0000-0002-4563-1960

Shulin Chen – Changsha Semiconductor Technology and Application Innovation Research Institute, College of Semiconductors (College of Integrated Circuits), Hunan University, Changsha 410082, China; orcid.org/0009-0007-2536-2074

Shanshan Tao – Department of Chemistry, Faculty of Science, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore; orcid.org/0000-0002-1973-0543

Masaki Takeguchi – National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan; orcid.org/0000-0002-0282-6020

Author Contributions

D.J. conceptualization, funding acquisition, writing, drawing, review & editing. J.L., X.T., S.C., and M.T. TEM observations. S.T. COF sample preparations. Y.L. In-situ PXRD characterization. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no conflict of interest.

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