Two-dimensional covalent organic framework films prepared on various substrates through vapor induced conversion

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Covalent organic frameworks (COFs) can exhibit high specific surface area and catalytic activity, but traditional solution-based synthesis methods often lead to insoluble and infusible powders or fragile films on solution surface. Herein we report large-area -C=N- linked two-dimensional (2D) COF films with controllable thicknesses via vapor induced conversion in a chemical vapor deposition (CVD) system. The assembly process is achieved by reversible Schiff base polycondensation between PyTTA film and TPA vapor, which results in a uniform organic framework film directly on growth substrate, and is driven by π-π stacking interactions with the aid of water and acetic acid. Wafer-scale 2D COF films with different structures have been successfully synthesized by adjusting their building blocks, suggesting its generic applicability. The carrier mobility of PyTTA-TPA COF films can reach $1.89 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$. When employed as catalysts in hydrogen evolution reaction (HER), they show high electrocatalytic activity compared with metal-free COFs or even some metallic catalysts. Our results represent a versatile route for the direct construction of large-area uniform 2D COF films on substrates towards multi-functional applications of 2D π-conjugated systems.
Covalement organic frameworks (COFs), a class of crystalline porouupermaterials, have gained rapid recognition of the researchers due to their well-defined porosity, interconnected structures, and good chemical stability. Based on these advantages, COFs enable the implementation of chemical and structural control for promising applications in the field of gas storage, proton conduction, and sensing. In particular, two-dimensionally linked π-conjugated COFs (2D-COFs) having an adjustable electronic band gap are a new generation of semiconducting materials for electronics.

The structures of 2D-COFs, which are chemically bonded by boronate, boroxine, hydrozarene, and imine linkages, contain well-defined framework. The light elements (N, O, S) can be embedded in the structures via quantitative post-modification or they can be introduced into the skeletons via the bottom-up synthesis. Furthermore, synthetic 2D organic frameworks composed of N atoms exhibit outstanding properties and functions, and have emerged as a highly tunable alternative to metal catalysts for oxygen reduction reaction (ORR).

In recent years, a variety of methods including solvothermal methods, ultrasonic methods, mechanical grding and on-surface synthesis techniques have been developed for the synthesis of COFs via all of the common linkages (including imine) targeting specific practical applications. Two-dimensional COF particles with grain sizes of micrometers were yielded via seeded growth in solution. However, it is difficult to disperse these crystalline particles fully in solution for uniform growth. Instead, single-crystal metals and graphite have also been demonstrated to be able to grow COF grains up to tens of nanometers in ultra-high vacuum.

The selective growth of imine-linked COF is achievable via the condensation reaction between organic or inorganic –CHO and –NH2. However, the synthesis of COF films based vapor-induced film conversion is significantly more complicated than the process in solution or at air/liquid interface. Organic monomers are in the form of single molecules in solution that can adjust their direction and angle freely during the construction of crystalline COFs, but interaction forces between the neighboring molecules in PyTTA films would inevitably limit the reactivity between the –NH2 and –CHO functional groups. In the presence of only TPA and PyTTA, annealing of a composite membrane did not result in crystalline PyTTA COF films. However, small molecules can intercalate into the molecule space of organic film, and weak the van der Waals interaction between neighboring monomers. Figure 1b–e showed the topography change of PyTTA surface. The intrinsic PyTTA film prepared by thermal evaporation is characterized by a closely packed powder (Fig. 1b). In the presence of acetic acid and H2O, its surface undergoes significant modifications with continuous flattening after growth (Fig. 1c–e).

Characterizations of PyTTA-TPA COF films. Various substrates such as SiO2/Si, glass, Cu foil, and so on have been used to grow PyTTA-TPO COF films. The thickness of the films can be easily controlled from several nanometers to tens of nanometers by adjusting the pre-arranged...
PyTTA films (Supplementary Figs. 3, 17, and 18). Because the growth occurs on substrate surface at atmospheric pressure, it follows that patterning PyTTA film through a shadow mask will promote the growth of COF patterns (Fig. 2b and Supplementary Fig. 19), which is compatible with current silicon processing techniques and highly desired for 2D electronics. Figure 2c shows a high-magnification optical microscopy image of the COF film. The uniform color contrast indicates the film is of uniform thickness, as is also confirmed by scanning electron microscope (SEM) observation (Supplementary Fig. 20). Atomic force microscopy (AFM) was used to measure the detailed feature of the PyTTA-TPA COF film (Fig. 2d), which indicated a smooth surface (Ra = 0.731 nm) with a step height of 2.2 nm, corresponding to few-layer 2D COFs.

XPS survey spectrum of the PyTTA-TPA COF film shows the presence of carbon and nitrogen along with the signals of Si and O from the SiO2/Si substrate (Supplementary Fig. 21). The C1s XPS spectrum can be divided into several major peaks centered at around 283.5 eV, 284.8 eV, 285.8 eV, and 288.2 eV (Fig. 2e), which correspond to the C=N, C–C/C=C, C–N, and C=N, respectively, with a graphite-like structure. Similarly, the high-resolution XPS spectrum of N 1s is composed of two peaks which are centered at around 399.4 and 398.9 eV (Fig. 2f), and can be assigned to the N of the unreacted amine groups in PyTTA and the N in imine bonding structure, respectively. According to the FT-IR spectra (Fig. 2g), adsorption bands of the −NH2 groups of PyTTA located at 3334 and 3231 cm−1 disappear after growth with the subsequent appearance of a peak at 1624 cm−1, corresponding to the C=N stretching modes of imines, indicating the formation of −C=N− linkages in the PyTTA-TPA COFs (Fig. 2g). Based on the change of C=N: −NH2 peak intensity, it is easy to understand that the condensation reaction between amines and aldehydes is enhanced with the extension of reaction time (Supplementary Figs. 22–24).

For further analysis of the structure and uniformity of the COF films, Raman spectra were measured using a confocal Raman microscope. Compared with those of PyTTA and TPA precursors, a broad band from 1660 cm−1 to 1720 cm−1 corresponds to the aldehyde C=O stretching vibration, while the band at 1364 cm−1 is derived from the stretching vibration of −NH2.

Fig. 1 Growth and structure. a Schematic representation for the growth of imine-linked 2D COF films on SiO2/Si substrates. b AFM image of a 7-nm-thick PyTTA film prepared by thermal evaporation. The average roughness (Ra) is 1.96 nm. c–e AFM images of PyTTA-TPA COF films grown at different growth times. c 7 h, Ra = 1.53 nm. d 14 h, Ra = 0.97 nm. e 15 h, Ra = 0.73 nm. Scale bar 2 μm.
The appearance of strong peaks at 1591 cm$^{-1}$ and 1618 cm$^{-1}$ correspond to the stretching vibrations of the aromatic C=C groups and the imine moieties, respectively, indicating the formation of the imine bond linking unit$^{39}$. Spatial dependences of the intensity of the characteristic Raman peak at 1591 cm$^{-1}$ were plotted in Fig. 2i and Supplementary Fig. 25. The uniform color intensity is a reliable indicator of the uniform thickness. The UV-Vis spectrum of PyTTA-TPA COF film shows a broad absorbance mainly in the range from 250 and 600 nm, which is designated as the $\pi$-$\pi$ transition (Supplementary Fig. 26). The energy band gap is ~1.87 eV, calculated from the UV-Vis edge absorption (Supplementary Fig. 27), and the lowest unoccupied molecular orbital (LUMO) measured by cyclic voltammetry (CV) is $-3.73$ eV (Supplementary Fig. S28). Combining the energy band gap and LUMO level, the highest occupied molecular orbital (HOMO) energy level calculated is around $-5.60$ eV, suggesting the semiconducting character of the PyTTA-TPA COF film (Supplementary Fig. 29).

Grazing-incidence wide-angle X-ray scattering (GIWAXS) was used for characterization of the crystal structure of PyTTA-TPA COF films, and the crystallographic information of PyTTA-TPA COF film was obtained by Pawley refinement of film diffraction signal (Fig. 3a, b). According to the Pawley refinement results (Fig. 3b and Supplementary Table 1), the PyTTA-TPA COF belonged to the C2/m space group with unit cell parameter of $a = 2.5$ nm, $b = 2.4$ nm, and $c = 0.4$ nm. $\alpha = 90^\circ$, $\beta = 91^\circ$, and $\gamma = 90^\circ$. Three prominent diffraction peaks at $2\theta = 3.7^\circ$, $\sim 7.5^\circ$ and $\sim 23.4^\circ$ can be assigned to the (100), (200) and (001) facets, respectively$^{42}$. The presence of a high intensity peak at $3.7^\circ$ is associated with the periodicities in (100) plane and is indicative of a well-defined ordered columnar array. The crystal size of the PyTTA-TPA COFs is ~26.8 nm by Scherrer’s analysis, which is comparable to that of PyTTA-TPA COF powders (~22.0 nm) synthesized by solvothermal method (Supplementary Fig. 30).

The 2D GIWAXS in Supplementary Fig. 12 showed an arc pattern, and no orientation was found in the COF film, which indicated the crystallization process of irregular polygons to layered frameworks with ordered pores was driven by $\pi$-$\pi$ stacking interactions of adjacent sheets$^{41}$. However, on highly oriented pyrolytic graphite (HOPG) (Supplementary Fig. 31), the drastic change in intensity of the (001) signal in the directions proves the formation of oriented COF crystalline regions that
preferably lie with the $ab$ plane parallel to the HOPG surface.\(^4^3\) The results indicated that PyTTA and TPA precursors can move/rotate on substrates for COF assembly at the aid of $H_2O$ (Supplementary Fig. 9). Transmission electron microscopy (TEM) provides the most direct evidence of the microstructure of the COF film with the grain size reaching 50 nm (Fig. 3c).

High-resolution TEM (HRTEM) (Fig. 3d, e) demonstrates a clear quadrilateral network structure with a pore size of $\sim$2.45 nm (Fig. 1a), which is also consistent with the calculated pore size of PyTTA-TPA COFs by GIWAXS (Fig. 3b).

To check the generality of the CVD-based approach for growing 2D COF films, the synthesis of two other COFs based on PyTTA-BPyDCA and PyTTA-BPDA were studied (Fig. 4 and Supplementary Fig. 32). Except for the use of BPyDCA and BPDA instead of TPA as precursors, the growth procedure and parameters were similar to those of PyTTA-TPA COF films. Raman, XPS, and FTIR measurements verified the formation of imine bonds (Supplementary Figs. 33–35). As compared to the PyTTA-TPA COF, lattice constant of $\sim$2.8 nm was observed for PyTTA-BPyDCA COF films (Figs. 4b and 1a)\(^4^4\), which is consistent with the crystal plane along the (001) direction of the theoretical simulation structure. The two-dimensional slices with an interplanar spacing of $\sim$0.43 nm indicate a highly ordered arrangement in the COF film (Fig. 4e). GIWAX data of PyTTA-BPyDCA and PyTTA-BPDA films matches the theoretical calculation (Fig. 4c, f and Supplementary Tables 2 and 3). The peaks located at $\sim$3.2°, $\sim$6.4° are assigned to the (100) and (200) facets, respectively\(^4^4\).

**Electrical performance.** Imine-linked COFs, a class of $\pi$-conjugated semiconducting polymer, have a porous, well-defined network with large surface area, which is suitable for the applications in electronics and catalysts.\(^1^4\) To study the electronic properties of the COF films in field-effect transistors (FETs), 30 nm PyTTA-TPA COF films were grown in situ on a OTS-modified SiO$_2$/Si substrate\(^4^5$–$4^7$), which act as the active layer, while gold was used as the source and drain electrode for the device (Fig. 5a, b, Supplementary Figs. 36–38). Self-assemble OTS monomers have proved to be excellent candidates for ultra-thin gate dielectric layers in organic field-effect transistors (OFETs)\(^4^8$–$5^1$).

In the $I_{DS}$–$V_{DS}$ characteristic curve, the device exhibited a saturation current of $\sim$9.0 $\times 10^{-7}$ A at a gate voltage of $\sim$40 V, and the threshold voltage is $\sim$5 V (Supplementary Fig. 39a). In Fig. 5c, the $I_{DS}$–$V_G$ characteristics for the device in N$_2$ show a rapid increase of the source-drain current ($I_{DS}$) with the increase of negative gate voltage ($V_G$). The transistor exhibits a p-channel behavior with a hole mobility of $\sim$1.89 $\times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ estimated from the saturation current, and a high on/off ratio of $10^5$. The mobility is three orders of magnitude higher than that of previously reported imine-linked 2D...
conjugated COF film because the direct growth of COF films on SiO₂/Si substrates avoided the damage of films caused by transfer. Notably, the value is also significantly higher than that of PyTTA precursors (Supplementary Fig. 40), indicating the transport is due to COF lattice, not just hopping between unreacted precursor molecules. According to four-probe measurements, the conductivity of the film is ~8.40 × 10⁻⁶ S/cm (Supplementary Fig. 41). Generally, grain boundaries in semiconductor thin films will trap carriers, resulting in a decrease in the number of movable carriers. Therefore, an appropriate reduction in channel length will help improve device performance (Fig. 5d and Supplementary Fig. 42). Additionally, we have drawn a histogram based on the carrier mobility data of 20 FET devices (Fig. 5e), confirming the uniformity of the COF film quality.

To further explore the potential applications of the porous 2D COF films, the electrocatalytic activities of PyTTA-TPA, PyTTA-BPyDCA, and PyTTA-BPDA COF films directly grown on copper electrodes were evaluated towards HER in acidic (0.5 M H₂SO₄) aqueous solution (Fig. 5f). The results of the linear sweep volt ampere curves indicated negligible electrocatalytic activity of the bare copper substrate, as reflected by the higher overpotential and lower current density, while better catalytic activity was shown by the three COF films. In presence of ~10 mA cm⁻² as the driving current density, the respective HER onset potentials of PyTTA-TPA, PyTTA-BPyDCA, and PyTTA-BPDA COF films were 235, 208, and 268 mV while the overpotential values were 359, 315, and 438 mV, respectively (Fig. 5f). However, the electrocatalytic activity of pure graphene and PyTTA precursors is negligible, indicating that the COF structure is mainly responsible for the observed electrocatalytic effect. These results are better than those of metal-free COFs, and compare favorably with those obtained using some traditional metal catalysts, indicating extraordinary activity toward HER. In our experiments, we observed an increasing trend of the onset potential from PyTTA-BPyDCA to PyTTA-TPA and to PyTTA-BPDA COF (Fig. 5g). DFT calculations were performed to investigate the origin of HER performance of these COFs. Our results showed that the free energy changes for the HER of various N sites of these COFs at equilibrium potential (0 V) are comparable with each other and are all close to 0 eV (Supplementary Fig. 43, calculation details were provided in SI), suggesting the high HER performance of these COFs.

Electrochemical impedance spectroscopic (EIS) measurements are studied to investigate the electrode dynamics from the change of impedance with the frequency of sine wave. Figure 5i shows the Nyquist plots of the COF film-based catalysts within the frequency range of 0.01 Hz to 100 kHz at ~50 mV vs RHE. The semicircular outline indicates a kinetically controlled electrochemical reaction on the electrode surface. The calculated charge-transfer resistance (Rct) for the PyTTA-BPDA, PyTTA-TPA, and PyTTA-BPyDCA COF films was ~45.8, ~38.9, and ~31.5 Ω, respectively, which is smaller than that of some reported metal-free catalysts, suggesting rapid charge-transfer in the imine-linked COFs. To investigate the durability of the COF film, we performed long-term potential cycling test under the potential range of 0 V to ~0.8 V vs RHE at a scan rate of 1 mV s⁻¹. After 1000 cycles, the activity of the PyTTA-TPA film remained unchanged with respect to the current density at the onset potential or different potentials (Fig. 5j), suggesting high stability of the PyTTA-TPA film. The high HER catalytic activity may originate...
from the perfect contact to Cu electrode. Due to the absence of adhesives, contact resistance will be reduced by creating a clean interface, and thus promoting the electronic transmission between the catalyst and electrode. The vapor-induced approach provides uniform and stable COF films grown on electrodes, leading to a highly adjustable catalytic platform for HER (Fig. 5k).

**Discussion**

In summary, we demonstrated a vapor-induced process for synthesizing high-quality 2D PyTTA-TPA, PyTTA-BPyDCA, and PyTTA-BPDA COF films on a large scale. Despite the topological limitations from the perspective of close-packed molecular arrangement, the thermodynamic control of the crystal structure is increased due to increasing reversibility of the Schiff base reaction in the presence of acetic acid and H2O. These COF films can be grown on various substrates and can be directly used for device fabrication, thus avoiding the problems of film contamination and breakage associated with the preparation of films by traditional solution-based methods. TEM, AFM, and GIWAXS measurements illustrated high quality of these COF films with the carrier mobility up to 1.89 x 10^-3 cm^2 V^-1 s^-1 and a high on/off ratio of 10^5. When used as active materials for HER, the COF films show low onset potentials and overpotentials with high stability. This work contributes a general vapor-induced method...
for producing large-area 2D COF films with direct relevance to FETs and HER. Our work further points to the possibilities of using the method for the growth of other 2D COFs, which is important for basic research and practical applications.

**Methods**

**Preparation of PyTTA film.** PyTTA film was deposited on SiO$_2$/Si, glass. Cu foil and so on via thermal evaporation. In all, 20 mg PyTTA powders were placed into a crucible in an inert gas evaporative system, and growth substrates were loaded with their face down to the PyTTA source. PyTTA can be patterned on substrates by using a shadow mask. When the vacuum reaches 8×10$^{-6}$ mbar, the temperature rises to 130 °C at a rate of 20 °C/min, and then slowly rises to 180 °C at a rate of 5 °C/min. The evaporation rate was maintained at 0.1 Å/s, and the thickness of PyTTA film can be controlled by deposition time.

**Synthesis of 2D COF films.** PyTTA-TPA, PyTTA-BPyDCA, and PyTTA-BPDA COF films were grown on various substrates by vapor-induced conversion in a CVD system. The growth substrates with PyTTA films on their surface were placed in the middle of the 2-inch quartz tube, which was installed in the tube furnace. TPA (or BPyDCA, BPDA) powders were placed in a separate ceramic boat at the upper stream side. The tube furnace is externally connected with a bubbler to hold hydrogen and argon flow of 10 sccm and 10 sccm is used as carrier gas. The center heating zone was heated to 140 °C. Note that the temperature of the TPA (or BPyDCA, BPDA) powders is controlled at (105 °C for BPyDCA, 110 °C for BPDA) when the center heating zone reaches 140 °C. After a 7-day growth, the central heating zone was heated to 180 °C for 1 h to remove unreacted TPA (or BPyDCA, BPDA) precursors. The furnace was then cooled to room temperature to obtain COF films.

**Characterizations of 2D COF films.** Film morphology was imaged using a NIKON Eclipse LV-100 optical microscope. The material structure of COF films was studied by using a Horiba Raman spectroscope with laser excitation at 532 nm. A semiconductor detector (Pilatus 300 K, DECTRIS, Switzerland) was studied by using a Horiba Raman spectroscope with laser excitation at 532 nm.

**Electrochemical measurements.** Electrochemical measurements were conducted using a CHI 760E electrochemical station via the standard three-electrode electrochemical system. A COF film grown on a piece of Cu foil is used as working electrode, and an Ag/AgCl (saturated KCl) electrode and a piece of Pt foil are used as reference electrode and counter electrode respectively. The film thickness is ~13 nm. Before the electrochemical measurement, the electrolyte (0.5 M H$_2$SO$_4$) was purged with pure N$_2$ for 30 min to eliminate dissolved oxygen. HER activities were carried out by linear sweep voltammetry (LSV) with a scan rate of 0.1 mV/s. The potentials were calibrated to the reversible hydrogen electrode (RHE) according to the Nernst equation ($E_{RHE} = E_{Ag/AgCl} + 0.0591 \, pH + 0.2412 \, V_{Ag/AgCl}$) and iR corrected. EIS measurements were conducted at the open-circuit voltage from 1000 kHz to 0.01 Hz with an amplitude of 10 mV.

**Data availability**

The authors declare that the experimental data supporting the results of this study can be found in the paper and its Supplementary Information file. The experimental results of the study along with other simulation data are provided in the Supplementary Information file. The detailed simulation file for the study are available from the corresponding author upon request.

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Author contributions

J.C. and Y.Q.L. designed and supervised the project. M.L. carried out the experiments. J.C. and Y.Q.L. wrote the manuscript. All the authors participated in discussions of the research.

Competing interests

The authors declare no competing interests.

Additional information

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