

Angewandte International Edition www.angewandte.org

Hydrogen-Bonded Organic Frameworks Hot Paper

## A Solution-Processable Porphyrin-Based Hydrogen-Bonded Organic Framework for Photoelectrochemical Sensing of Carbon Dioxide

Chen Wang, Xiyu Song, Yao Wang, Rui Xu, Xiangyu Gao, Cheng Shang, Peng Lei, Qingdao Zeng, Yaming Zhou, Banglin Chen,\* and Peng Li\*

Abstract: Detecting CO<sub>2</sub> in complex gas mixtures is challenging due to the presence of competitive gases in the ambient atmosphere. Photoelectrochemical (PEC) techniques offer a solution, but material selection and specificity remain limiting. Here, we constructed a hydrogen-bonded organic framework material based on a porphyrin tecton decorated with diaminotriazine (DAT) moieties. The DAT moieties on the porphyrin molecules not only facilitate the formation of complementary hydrogen bonds between the tectons but also function as recognition sites in the resulting porous HOF materials for the selective adsorption of CO<sub>2</sub>. In addition, the in-plane growth of FDU-HOF-2 into anisotropic molecular sheets with large areas of up to  $23000 \,\mu\text{m}^2$  and controllable thickness between 0.298 and 2.407 µm were realized in yields of over 89% by a simple solution-processing method. The FDU-HOF-2 can be directly grown and deposited onto different substrates including silica, carbon, and metal oxides by self-assembly in situ in formic acid. As a proof of concept, a screen-printing electrode deposited with FDU-HOF-2 was fabricate as a label-free photoelectrochemical (PEC) sensor for CO<sub>2</sub> detection. Such a signaloff PEC sensor exhibits low detection limit for CO<sub>2</sub> (2.3 ppm), reusability (at least 30 cycles), and long-term working stability (at least 30 days).

[\*] C. Wang, X. Song, Y. Wang, R. Xu, X. Gao, Prof. C. Shang, Prof. Y. Zhou, Dr. P. Li

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University 2005 Songhu Road, Shanghai 200438 (China) E-mail: penglichem@fudan.edu.cn

P. Lei, Q. Zeng

CAS Key Laboratory of Standardization and Measurement for Nanotechnology, CAS Center for Excellence in Nanoscience, Department of Chemistry and International Institute of Nanotechnology, National Center for Nanoscience and Technology (NCNST)

No. 11 Beiyitiao, Zhongguancun, Beijing 100190 (China) Prof. B. Chen

Fujian Provincial Key Laboratory of Polymer Materials, College of Chemistry and Materials Science, Fujian Normal University Fuzhou 350007 (China)

E-mail: banglin.chen@fjnu.edu.cn banglin2010@gmail.com

Angew. Chem. Int. Ed. 2023, e202311482 (1 of 9)

#### Introduction

Carbon dioxide  $(CO_2)$  is a ubiquitous molecule known for its non-toxic, benign, cost-effective, highly oxidizing, and predominantly inert properties.<sup>[1]</sup> Detection and monitoring of CO<sub>2</sub> hold paramount significance in investigating and understanding the multiple facets of this molecule, as well as in occupational health, public health, and societal welfare.<sup>[2]</sup> However, CO<sub>2</sub> sensing in a mixture of multiple gases proves challenging due to the presence of competitive gases such as oxygen, carbon monoxide, and water vapor, all of which exhibit considerably higher chemical reactivity.<sup>[3]</sup> Currently, a variety of modalities and materials are available for the detection and monitoring of CO<sub>2</sub>, including electrochemical (EC) sensors,<sup>[4]</sup> fluorescence analysis,<sup>[5]</sup> non-dispersive infrared sensors,<sup>[6]</sup> semiconducting field effect transistors (FETs),<sup>[7]</sup> paper-based sensors<sup>[8]</sup> and polymers.<sup>[9]</sup> Despite the diversity and efficiency of these methods, they do not provide a viable solution for CO<sub>2</sub> sensing in complex environments, and the devices require fabrication of complex equipment and processes.

Photoelectrochemical (PEC) technique, with their operating simplicity, compact size, cost-effectiveness, rapid reaction time and great sensitivity offer a possible solution to these limitations.<sup>[10]</sup> In contrast to conventional electrochemical techniques, due to the separation of excitation signal and output signal, PEC assay possesses low background signal, which reduces the background interference.<sup>[11]</sup> PEC analytical methods have gained widespread application in detecting various targets, such as bacteria, proteins, nucleic acids, small molecules, and metal ions.[12] Importantly, the efficacy of PEC methods critically hinges upon the semiconductor materials for the photoelectrode, and an array of photoactive semiconductor materials has been developed for PEC sensors, including metal oxide (TiO<sub>2</sub>, ZnO),<sup>[13]</sup> metal sulfides compound  $(Bi_2S_3, Ag_2S)^{[14]}$  and nanocomposite materials (AuNRs@TiO<sub>2</sub>, Bi<sub>2</sub>S<sub>3</sub>/TiO<sub>2</sub>).<sup>[15]</sup> However, among various photoactive materials such as TiO<sub>2</sub> and ZnO only provide surface chemical recognition, and molecules with similar structures to target molecules confound the detectors and result in false alarms. The ordered porous materials are considered to be far superior to nonporous materials for sensing due to their high reactive surface area, unique size discrimination, and siterecognition.[16]

Hydrogen-bonded organic frameworks (HOF) belong to a branch of porous molecular crystals with extrinsic porosities caused by the imperfect packing.<sup>[17]</sup> HOFs have recently become a focus of supramolecular materials and have evolved rapidly into a family of stable and functional crystalline porous materials based on the combining of multiple intermolecular complementary hydrogen-bonds and other synthetic strategies.<sup>[18]</sup> Among various types of HOFs, porphyrin-based tectons and their metallated derivatives have been used widely to construct functional HOF materials for applications associated with gas separation,<sup>[19]</sup> sensing,<sup>[20]</sup> catalysis<sup>[21]</sup> and drug delivery.<sup>[22]</sup> Remarkably, porphyrin is an aromatic macrocycle with an  $18-\pi$  electron framework, the wide absorption range covering the visible to NIR region endows porphyrin-based materials with outstanding panchromatic light harvesting ability,<sup>[23]</sup> further allow for accelerating electron transfer rate for improved PEC performances of porphyrin-based HOFs. Amidst a myriad of distinct strategies employed in constructing HOFs, shape-fitted  $\pi$ - $\pi$  stacking strategy is one of the most efficient methods to construct stable HOFs.<sup>[24]</sup> Numerous HOF materials have been prepared based on tectons containing both organic backbones with large  $\pi$ -conjugated structures and chemically grafted hydrogen-bonding sites such as diaminotriazine (DAT), carboxylic acids and ureas.<sup>[25]</sup> Furthermore, the incorporation of the DAT moiety into the molecular architecture of HOFs not only facilitates the assembly of HOF crystal structures, but also imparts the capacity for chemical CO<sub>2</sub> adsorption to HOFs, because the gas inserts into the HOFs to form chains of oxygen-bound carbamate species with DAT. Such an amine binding orientation, coupled with a synergistic arrangement of porous structures, grants unfettered access to  $CO_2$  at the amine sites, facilitating robust chemisorption.<sup>[26]</sup>

Here, we report a photosensitive and highly conductive two-dimensional (2D) hydrogen-bonded porphyrin framework, FDU-HOF-2. The HOF could be fabricated into sheet-like crystals with large areas (up to 23500  $\mu$ m<sup>2</sup>), controllable thickness (0.298–2.407  $\mu$ m) and high area to thickness ratio (up to 9791) by a facile solution-processing method. Importantly, the DAT groups in the HOFs serve as the selective recognition sites for CO<sub>2</sub>. The screen printing electrodes deposited with FDU-HOF-2 show highly selective CO<sub>2</sub> detection performance with wide sensing range (5– 400 ppm), an extremely low detection limit (2.3 ppm) and exceptional specificity.

### **Results and Discussion**

5,10,15,20-Tetrakis(4-(2,4-diaminotriazinyl)phenyl)porphyrin (H<sub>2</sub>TDPP) and its precursor, 5,10,15,20-tetrakistetra(4cyanophenyl)porphyrin were synthesized according to previously reported methods.<sup>[20,27]</sup> We prepared a HOF crystal (hereafter FDU-HOF-2) with H<sub>2</sub>TDPP as the monomer by using DMF/acetone mixed solvents (Figure 1a). In the crystal structure of FDU-HOF-2, the H<sub>2</sub>TDPP monomer interact with one another by  $\pi$ - $\pi$  stacking at 3.551 Å (Figure 1b) to form a dimer, where the H<sub>2</sub>TDPP molecule connects to another H<sub>2</sub>TDPP molecule in a head-to-head orientation, with hydrogen bond lengths of 2.928 and



*Figure 1.* Crystal structure of FDU-HOF-2. a) Schematic representation of the synthesis procedure and structure. b) The adjacent building unit from two independent networks forms multiple face-to-face  $\pi$ - $\pi$  stacking interactions at 3.551 Å. c) Adjacent organic building units are linked together with hydrogen bond lengths of 2.928, 3.081 and 2.959 Å (dotted black line). d) The host framework shows one-dimensional channels with an elliptical window aperture of 11.97×21.74 Å along the crystallographic <100> direction. e) *pcu* topology network as it occurs in the crystal structure.

Angew. Chem. Int. Ed. 2023, e202311482 (2 of 9)

© 2023 Wiley-VCH GmbH



2.969 Å in one direction. Similarly, it is also linked to another H<sub>2</sub>TDPP molecule in a side-to-side manner, with hydrogen bond lengths of 3.027 and 3.081 Å, thus creating a 2D network structure. Furthermore, in a different direction, H<sub>2</sub>TDPP can form connections with other H<sub>2</sub>TDPP molecules in a head-to-head orientation, forming hydrogen bonds with a length of 2.959 Å, facilitating the linkage of 2D networks into a cohesive three-dimensional (3D) structure (Figures 1c, Table S1, S2). Ultimately, this arrangement results in the formation of a HOF frameworks with a primitive cubic (*pcu*) topology along the z-axis with a pore size of ca. 11.97×21.74 Å (Figures 1d, 1e). The solventaccessible void of FDU-HOF-2 estimated by PLATON is approximately 53.1 % (Figure S1).<sup>[28]</sup>

The crystalline nature of FDU-HOF-2 was demonstrated with a powder X-ray diffraction (PXRD) investigation (Figure 2a). The PXRD pattern for FDU-HOF-2 features the characteristic peaks at 3.49°, 4.58° and 6.92°, which coincide well with the simulated pattern of FDU-HOF-2. The excellent match of the peak positions confirms the phase purity of the FDU-HOF-2 crystals. However, the elimination of solvent guests from the pores gave rise to the activated FDU-HOF-2 and the <0 0 1> crystal plane of FDU-HOF-2 was shifted, indicating that the framework is

slightly contracted. Encouraged by the excellent stability and suitable pore size of FDU-HOF-2, we further investigated the permanent porosity behavior of a guest-free sample. Before the gas sorption measurement, the activation of acetone-exchanged crystals in a high vacuum provided an activated sample at room temperature. The pore characterization was explored with 196 K and 298 K CO<sub>2</sub> adsorption isotherms (Figure 2b, 2c). Interestingly, FDU-HOF-2 displays reversible CO<sub>2</sub> adsorption and desorption isotherms at 196 K, and the CO<sub>2</sub> sorption isotherm shows a very sharp uptake in the low-pressure region ( $P/P_0 < 0.08$ ), an indication of a robust microporous feature. The Brunauer-Emmett-Teller surface area of FDU-HOF-2 was determined to be  $250\ m^2g^{-1}$  by the  $CO_2$  sorption experiment at 196 K. And the permanent porosity and channel in FDU-HOF-2 prompted us to further explore its CO<sub>2</sub> selective absorption performances. Hence, low-pressure single-component sorption data of CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> were collected at 298 K. FDU-HOF-2 shows uptake amounts of 25.8, 1.35 and 2.71 cm<sup>3</sup>/g for CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> at 298 K and 100 kPa, respectively. To further explore the gas affinity, the adsorption heat  $(Q_{st})$  for CO2 was calculated based on the isotherms measured at 273 K and 298 K using the Clausius-Clapeyron equation. The corresponding  $Q_{\rm st}$  value of FDU-HOF-2 at nearly zero



**Figure 2.** a) Comparison of the XRD patterns of as-synthesized FDU-HOF-2 and simulated pattern. b) 196 K CO<sub>2</sub> adsorption isotherms of FDU-HOF-2. c) 298 K CO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> adsorption isotherms of FDU-HOF-2. d) Schematic presentation of the combination of FDU-HOF-2 and CO<sub>2</sub>. SEM images of sheet FDU-HOF-2 with different diffusion times: (e, g) 2 h and (f, h) 8 h.

Angew. Chem. Int. Ed. 2023, e202311482 (3 of 9)

© 2023 Wiley-VCH GmbH

coverage for  $CO_2$  was 25.7 kJ/mol (Figure S2). The results demonstrate the presence of a strong interaction between the  $CO_2$  substrates and the framework. As has been discussed in the literature, the exposure of  $CO_2$  to FDU-HOF-2 leads to the formation of carbamic acid, as evidenced by the characteristic peaks of both physically and chemically absorbed  $CO_2$  in the solid-state <sup>13</sup>C NMR spectra (Figure 2d, S3).<sup>[29]</sup> This occurs through reversible reactions, exchange and generation of a dynamic system of species, indicating the potential sensing performance of FDU-HOF-2 for  $CO_2$ .

Although chemical or physical exfoliation methods have been used to prepare nanosheets from bulky HOF crystals with low yields,<sup>[30]</sup> the bottom-up approach for HOF nanosheets preparation has not been realized to date. Interfacial assembly of supramolecular mono- and bilayered molecular arrays with nanopores based on pre-designed synthons and complementary hydrogen-bonding has been achieved,<sup>[31]</sup> but control over the multi-layer assembly is difficult even on the surface.<sup>[32]</sup> To prepare homogeneous and stable 2D sheets materials, it is common practice to limit the crystal growth to a particular plane, for example, by growing thin layers of sheets on a specific template to prepare lamellar materials with structural orientation. Alternatively, it is possible to control the crystal growth in a specific crystal plane by using templating agents or surfactants to achieve crystallization in the 2D direction. In previous works of growing DAT functionalized porphyrin HOFs by adjusting the solvent led to different blocks of crystals.<sup>[27]</sup> In these blocks the porphyrin tectons, crystals without specific morphologies, self-assemble with each other by exploiting hydrogenbonding sites to form 2D sheets which were further extended to a 3D framework through intermolecular  $\pi$ - $\pi$ stacking. We reasoned that controlling the initial concentrations of precursors and combinations of good or poor solvents during the synthesis of HOF materials may result in size controlled, uniform and anisotropic HOF crystals. In this work, we synthesized sheet-like FDU-HOF-2 in high yield by a liquid/liquid diffusion method as follows: (1) the porphyrin monomer is fully dissolved in DMF, (2) a DMF solution containing the porphyrin monomer is mixed with a specific percentage of acetone to prepare the 2D HOF sheets through a simple recrystallization method at room temperature (Figure S4). Then, we varied the HOF precursor ratios and growth times to investigate the morphological characteristics of FDU-HOF-2. As the HOF crystals start to recrystallize, the color of the solution becomes lighter and microcrystals of HOFs appear in the bottle. After 24 h of crystallization, a large number of HOF sheets appear in the bottle and the color of the solution becomes almost transparent (Figure S5). Optical microscopy shows that the HOF crystals prepared by this liquid/liquid diffusion method display sheet crystals about a millimeter in size (Figure S6). Subsequently, we examined thegrowth process of HOF sheets by scanning electron microscopy (SEM). After 2 h of liquid/liquid diffusion, the size of HOF sheets is about 5 µm  $\times 5 \,\mu m$  and the thickness is about 295 nm. The sheet fragments also display regular shapes, indicating that the large sheets are formed by the gradual growth of small sheets (Figure 2e, 2g, S7). With 4 h of growth, the HOF

Angew. Chem. Int. Ed. 2023, e202311482 (4 of 9)

sheets grow to  $10 \,\mu\text{m} \times 20 \,\mu\text{m}$  and the thickness increase to 412 nm (Figure S8), and the HOF sheets are found to be fractured with regular rectangular shapes exhibiting straight perpendicular edges after 8 h growth, their size is about 40 µm×100 µm, thickness is about 1905 nm (Figure 2f, 2h, S9). After 24 h of growth, the size of an HOF sheet is about 100 µm×150 µm, and its thickness is about 2210 nm (Figure S10). According to the SEM results, as the diffusion time increased from 2 to 24 h, the area and thickness of the sheet FDU-HOF-2 continuously increased from 27 to  $23500 \,\mu\text{m}^2$  and from 0.298 to 2.407  $\mu\text{m}$ , respectively (Figure S11). However, after 24 h of growth, the area/thickness ratio continuously increased from 91 to 9791 with the diffusion (Figure S12), demonstrating that FDU-HOF-2 crystals recrystallized by the liquid/liquid method tend to grow in a sheet-shape rather thanforming blocks and rods. 2D materials are used in the field of gas detection, because their large specific surface area provides abundant active sites facilitating gas adsorption. Hydrogen-bonded organic frameworks, a typical porous crystalline material, has becoming a fascinating candidate with which to build sensing platforms possessing satisfactory gas sensing characteristics.

Integrating porous crystalline materials onto electronic devices and programming their nano-organizations on surfaces<sup>[33]</sup> notably broadens their scope of electrochemistry applications such as electrocatalysis and electrochemistry sensing.<sup>[34]</sup> Porous materials with sheet morphology are ideal for deposition on electronic devices because of the increased contact areas and the consequently reduced diffusion distance between electrolytes and the working interface.<sup>[35]</sup> However, during the modification of the electrode interface, the 2D sheets are liable to form a tight stacked structure, which is not conducive to the transmission of electrons and impedes the full access between the materials and gas molecules, so there is much progress to be made about their sensitivity and response and recovery characteristics. The in situ assembly of sheets on photoelectrochemical (PEC) sensors being an effective strategy to address the aforementioned issues, we utilized the tendency of porphyrins to form dimers and grow into 2D sheets on carbon, silicon wafers and indium tin oxide (ITO) via the natural evaporation of a formic acid solution containing porphyrin molecules. The layered structure of FDU-HOF-2 was easily observed from the SEM images (Figure S13). Then, we use this method to rapidly modify the screen-printing electrode (SPE) surface with consistent thickness nanosheets (NS) FUD-HOF-2, termed NS FDU-HOF-2/SPE (Figure 3a). For comparative analysis, sheet crystals of FDU-HOF-2 were prepared and used to modify the electrodes (termed sheet FDU-HOF-2/ SPE) by a drop casting method. We employed scanning tunneling electron microscopy (STM) to further investigate the self- assembly process of NS FDU-HOF-2. The STM results revealed that every two protonated porphyrins formed a dimer, and every four dimers constituted a latticelike structure. The angle of the lattice was approximately 90 degrees, and its width was 2.8 nm, which is consistent with the single crystal data. These findings elucidate the growth mechanism of two-dimensional lamellar HOFs via the in situ growth process (Figure 3b, 3c). To avoid energy-induced



**Research Articles** 





*Figure 3.* a) Schematic illustration of the fabrication process of NS FDU-HOF-2/SPE. b, c) Medium-scale and high-resolution STM of NS FDU-HOF-2 self-assembly structure at rt at the 1-heptanoic acid /HOPG interface. d, e) Structural profile of FDU-HOF-2 by low-electron-dose cryo-EM, and the FFT pattern of the selected area (inset) that was assigned to the FDU-HOF-2 crystal along the <010>, <020>, and <001> directions. f) Photocurrent responses of several MOFs (green), metal oxides (orange), HOFs (blue), COF-366 (red), and NS FDU-HOF-2/SPE (black). g) Photo-electrochemical response mechanism for the FDU-HOF-2/SPE.

structural damage and successfully visualize the crystallographic nature of the material, we used low-electron-dose cryo-EM to acquired rich microstructural details of FDU-HOF-2. A series of lattice planes along the <0 1 0>, <0 2 0>, <0 0 1>, <1 0 -1>, <0 1 1>, and <0 0 2> directions and the ordered 1D channel-like pores can be clearly witnessed, the FDU-HOF-2 crystals exhibited long-range order across the whole crystallite. The inverse fast Fourier transform (FFT) pattern more clearly presented the molecular assembly structure, in which each organic linker molecule interacts with four neighboring molecules through hydrogen bonds to extend into an intact two-dimensional structure with ordered rhombic aperture, in good agreement crystallographic with the theoretical aperture (11.97 Å×21.74 Å) (Figure 3d, 3e). The 2D HOFs structure can also be observed through atomic force microscopy (AFM), which measures the height of NS FDU-HOF-2 to be between 2.6 and 2.8 nm, and the structure of layer-bylayer stacked monolayer FDU-HOF-2 with the height

Angew. Chem. Int. Ed. 2023, e202311482 (5 of 9)

between 2.0 and 2.2 nm (Figure S14). The NS FDU-HOF-2 grown on SPE surface are directly studied via grazingincidence wide-angle X-ray scattering (GIWAXS). The reflections appear as rings because of the random orientation of the grains in the sample in contrast to the substrate. In detail, the reflection rings of NS FDU-HOF-2 at Qxy= 0.48 and 0.65  $Å^{-1}$  correspond to the lattice planes (Figure S15), which is consistent with the lattice planes of sheet FDU-HOF-2 (Figure S16). In summary, STM, cryo-EM and GIWAXS results indicate that the NS FDU-HOF-2 obtained by natural evaporation is the same as the sheet FDU-HOF-2 obtained by liquid/liquid diffusion. To gain a better understanding of the mechanism of acid induced selfassembly, we then performed DFT computation on FDU-HOF-2. The calculation details can be found in SI. For optimized FDU-HOF-2 crystal, the unit cell contains two molecules, each molecule having 6 hydrogen bonds. Based on the optimized structure, we then attempted to introduce formic acid into the cell to investigate how acid affects the

Angewandte

stability of the FDU-HOF-2 crystal. We consider both nitrogen atoms in porphyrin and melamine as potential sites for acidification and found that formic acid can strongly stabilize the melamine N with an adsorption energy of 20.0 kcal/mol by forming one OH···N hydrogen bond and three NH···O hydrogen bonds (Figure S17).

We then investigated the electrochemical and photoelectrochemical properties of NS FDU-HOF-2. The diffuse reflectance spectroscopy (DRS) experiments for NS FDU-HOF-2 indicate strong absorption bands from 300 to 500 nm (Figure S18). Based on the Tauc plots, we calculated the band gaps of FDU-HOF-2 to be 2.51 eV, based on the intersection of the section line and the abscissa (Figure S19). Next, we measured the photocurrent responses of sheet FDU-HOF-2/SPE and NS FDU-HOF-2/SPE using ascorbic acid as an electron donor and found that NS FDU-HOF-2/ SPE demonstrates the best photocurrent response ( $6 \mu A$ ) compared to the drop-coated sheet FDU-HOF-2/SPE  $(2 \mu A)$ , which is attributed to the ample contact between the material and the electrode surface, enabling rapid transfer of photoelectrons from the HOFs material to the electrode surface without complexing with holes (Figure S20). The interfacial properties of sheet FDU-HOF-2/SPE and NS FDU-HOF-2/SPE were investigated using electrochemical impedance spectroscopy (EIS). By using K<sub>3</sub>Fe(CN)<sub>6</sub>/K<sub>4</sub>Fe- $(CN)_6$  as redox probes, the semicircular segment of the Nyquist plot corresponds to a diffusion-controlled process, and its diameter is correlated with the charge-transfer resistance  $(R_{ct})$  of the sensing interface. The equivalent circuit was applied to calculate their  $R_{ct}$  values with the aid of a ZSimDemo software, the corresponding parameters  $(Zw, R_{cv}, Rs)$  have their conventional physical significance and are also listed here. The Nyquist plot obtained from sheet FDU-HOF-2/SPE shows a larger semicircle diameter (669.5  $\Omega$ ) than NS FDU-HOF-2/SPE (156.7  $\Omega$ ), meaning the charge transfer resistance increases (Figure S21). Additionally, we conducted a comparison of the photocurrent strength of FDU-HOF-2 with other conventional materials including COF-366, several MOFs, HOFs, and metal oxides, and discovered that FDU-HOF-2 manifests the highest photocurrent intensities under the same conditions (Figure 3f). The photocurrent response mechanism of FDU-HOF-2 is shown in Figure 3g. When the FDU-HOF-2 is excited to generate electron-hole pairs, the electrons of FDU-HOF-2 are transitioned from the valence band to the conduction band. Then, the electrons were transferred to the electrode to produce photocurrent readout and the photogenerated holes were captured by the electron donor ascorbic acid (AA) to promote the separation of photogenerated electron-hole pairs. The excellent photoelectrochemical properties of the nanosheet HOFs with the thickness of single- or few-atom layers is not only due to the intrinsic semiconductivity of the FDU-HOF-2, but also because of the minimized the transport length for the ions between FDU-HOF-2 and the electrode. To evaluate the stability of the NS FDU-HOF-2/SPE interface, we monitored the photocurrent response while turning the exciting light on and off in 10 s intervals. No obvious variation in the photocurrent response was observed after 30 cycles, demonstrating the stability of this PEC platform and absence of photobleaching during measurements (Figure S22).

To make the detection system more portable, a homemade portable photoelectric detection system using commercially available screen-printed electrodes (SPE) was constructed, in which the electrodes, gas pathway, electrolytic cell and wires are integrated into an acrylic template and connected to an electrochemical workstation (Figure 4a). The whole detection system is lightweight, highly integrated and portable, which provided potential commercial value for gas assay, and the schematic for the PEC sensor fabrication is depicted in Figure S23 in the Supporting Information. Next, we evaluated the sensing proficiency of the NS FDU-HOF-2/SPE sensor for CO<sub>2</sub> detection. Upon exposure to CO<sub>2</sub> at rt for 5 min, the electrode's photocurrent swiftly decreased from 6 µA to 1 µA. The formation of N-CO<sub>2</sub> on HOFs channel surface acts as an electron acceptor and captures the photoexcited electrons, thus leading to a decrease of current (photocurrent) in the channel, ultimately resulting in reduced photocurrents for these analytes (Figure S24).  $^{\left[ 16,36\right] }$  After purging with  $N_{2}$  and reheating to regenerate the pores, the photocurrent returned to a higher level (5.8  $\mu$ A). Subsequently, the sensor exhibited a rapid decline of photocurrent again upon exposure to CO<sub>2</sub>. Following multiple cycles, the sensor continued to display photocurrent changes in response to CO<sub>2</sub> passage, which demonstrates excellent recirculation performance of the PEC sensor (Figure 4b). In an EIS experiment, a consistent increase in the charge resistance from NS FDU-HOF-2/SPE was observed due to the exposure to CO<sub>2</sub> at different concentration: 0 ppm (156.7  $\Omega$ ), 5 ppm (258.4  $\Omega$ ), 100 ppm  $(706.6 \Omega)$  and 500 ppm  $(1993 \Omega)$  (Figure 4c, S25). Furthermore, we compared the photocurrent response of the NS FDU-HOF-2/SPE and sheet FDU-HOF-2/SPE towards CO<sub>2</sub>, and determined that the NS FDU-HOF-2/SPE exhibited the most impressive photocurrent response (4.89  $\mu$ A) compared with sheet FDU-HOF-2/SPE (0.98  $\mu$ A), and showed exceptional cycling performance (Figure 4d). Under the optimized conditions, the photocurrent response of the NS FDU-HOF-2/SPE sensor to different concentrations of CO<sub>2</sub> was investigated. The photocurrent decreases with increasing  $CO_2$  concentrations from 5 ppm to 400 ppm, and the photocurrent difference  $(\Delta I = I - I_0)$  before and after NS FDU-HOF-2/SPE treated with CO<sub>2</sub> have a good linear relationship with the CO<sub>2</sub> concentration. The regression equation could be fitted as follows:  $\Delta I = 0.00985 \ c \ (ppm) +$ 0.628 ( $R^2 = 0.988$ ), and the detection limit is 2.3 ppm (S/N = 3) (Figure 4e). The results show that the PEC sensor has a wide linear response range and a low detection limit for CO<sub>2</sub>. To be compared with the previously reported methods, the merits of the analytic characteristics for CO<sub>2</sub> determination are presented in Table S3. It is noteworthy that the PEC sensor exhibits good performances for CO<sub>2</sub> determination. The specificity of the PEC sensor is another important study, and we employed N2, H2O, O2, MeOH and EtOH as potential interferants to investigate the selectivity of the FDU-HOF-2/SPE based PEC sensor toward CO<sub>2</sub>. All these interferants were independently measured. Obviously, the  $\Delta I$  value for CO<sub>2</sub> is the maximum among all the tested

**Research Articles** 





**Figure 4.** a) Scheme for the fabrication of the PEC sensor decorated with FDU-HOF-2 and the process of  $CO_2$  sensing. b) Photocurrent response of  $CO_2$  with NS FDU-HOF-2/SPE. c) Photocurrent cycle response of  $CO_2$  using NS FDU-HOF-2/SPE and sheet FDU-HOF-2/SPE. d) Nyquist plots of NS FDU-HOF-2/SPE exposed to  $CO_2$  with different concentrations. e) The calibration curve for the  $CO_2$  determination using NS FDU-HOF-2/SPE. f) Photocurrent response of  $CO_2$  and interferents using NS FDU-HOF-2/SPE. g) The long-term storage stability of the PEC sensor.

materials, indicating good selectivity of the PEC sensor in determining  $CO_2$  (Figure 4f). We examined the long-term storage stability of the PEC sensor by comparing the photocurrent response variation towards  $CO_2$  before and after the sensor was stored in an argon-filled glove box for up to 30 days and observed only a 5.0% decrease in the photocurrent over this time, illustrating the excellent stability of this composite material (Figure 4g).

### Conclusion

In this work, we reported a facile bottom-up growth method to obtain 2D hydrogen-bonded porphyrin sheets with high yield (89%), large areas (up to 23500  $\mu$ m<sup>2</sup>), controllable thickness (0.298–2.407  $\mu$ m) and high area to thickness ratio (up to 9791). PXRD and CO<sub>2</sub> sorption isotherms confirm the crystallinity and microporosity of the FDU-HOF-2 sheets, respectively The HOF nanosheet grown in situ on the electrode exhibit wide range (5 - 400 ppm) and extremely low detection limit (2.3 ppm) for CO<sub>2</sub> gas detection, and the PEC sensor shows great reusability (at least 30 cycles), and long-term working stability (at least 30 days). This study could inspire the further development of solution-based bottom-up synthesis method of semiconductive HOF crystals with well-defined nanomorphology and greatly improve their device-processing related applications in the future.

#### Acknowledgements

P. L. gratefully acknowledges the financial support from the start-up fund of Fudan University and the fund of the State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University (KF2103). We thank the staff at BL17B1 beamline of the National Facility for Protein Science in Shanghai (NFPS), Shanghai Advanced Research Institute, CAS, for providing technical support in X-ray diffraction data collection and analysis.

### **Conflict of Interest**

The authors declare no conflict of interest.

#### Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Gas Detection  $\cdot$  HOF Nanosheets  $\cdot$  PEC Sensors  $\cdot$  In Situ Growth

- a) D. Zhang, Y. Fan, H. Chen, S. Trépout, M.-H. Li, Angew. Chem. Int. Ed. 2019, 58, 10260–10265; b) S. Lin, P. Theato, Macromol. Rapid Commun. 2013, 34, 1118–1133.
- [2] a) Y. Liu, Y. Tang, N. N. Barashkov, I. S. Irgibaeva, J. W. Y. Lam, R. Hu, D. Birimzhanova, Y. Yu, B. Z. Tang, J. Am. Chem. Soc. 2010, 132, 13951–13953; b) R. E. Kirk, D. F. Othmer, J. I. Kroschwitz, M. Howe-Grant, Encyclopedia of chemical technology, Vol. 10, Wiley, Hoboken, 1991.
- [3] J. J. Gassensmith, J. Y. Kim, J. M. Holcroft, O. K. Farha, J. F. Stoddart, J. T. Hupp, N. C. Jeong, J. Am. Chem. Soc. 2014, 136, 8277–8282.
- [4] M. Struzik, I. Garbayo, R. Pfenninger, J. L. M. Rupp, Adv. Mater. 2018, 30, 1804098.
- [5] S. M. Borisov, C. Krause, S. Arain, O. S. Wolfbeis, *Adv. Mater.* 2006, 18, 1511–1516.
- [6] R. K. Jha, IEEE Sens. J. 2022, 22, 6-15.
- [7] a) A. Bogomolova, CRC Press Boca Raton, FL, USA:, 2010;
  b) S. Neethirajan, D. S. Jayas, S. Sadistap, *Food Bioprocess. Technol.* 2009, 2, 115–121.
- [8] H. Wang, S. I. Vagin, B. Rieger, A. Meldrum, ACS Appl. Mater. Interfaces 2020, 12, 20507–20513.
- [9] J. Gong, M. Antonietti, J. Yuan, Angew. Chem. Int. Ed. 2017, 56, 7557–7563.
- [10] a) W.-W. Zhao, J.-J. Xu, H.-Y. Chen, *Chem. Rev.* 2014, 114, 7421–7441; b) W.-W. Zhao, J.-J. Xu, H.-Y. Chen, *Chem. Soc. Rev.* 2015, 44, 729–741; c) Y. Zhou, H. Yin, S. Ai, *Coord. Chem. Rev.* 2021, 447, 214156.
- [11] G. Abdi, L. Alluhaibi, E. Kowalewska, T. Mazur, K. Mech, A. Podborska, A. Sławek, H. Tanaka, K. Szaciłowski, *Coord. Chem. Rev.* 2023, 487, 215155.
- [12] a) F.-Z. Chen, X.-X. Fu, X.-J. Yu, Y.-H. Qiu, S.-B. Ren, Y.-C. Wang, D.-M. Han, W.-W. Zhao, *Anal. Chem.* 2023, *95*, 9052–9059; b) Y. Zheng, Y. Zhou, X. Cui, H. Yan, L. Cao, L. Gao, H. Yin, *J. Hazard. Mater.* 2022, *436*, 129146; c) Y. Zhao, J. Xiang, H. Cheng, X. Liu, F. Li, *Biosens. Bioelectron.* 2021, *194*, 113581; d) R. Hua, N. Hao, J. Lu, J. Qian, Q. Liu, H. Li, K. Wang, *Biosens. Bioelectron.* 2018, *106*, 57–63; e) K. Szaciłowski, W. Macyk, A. Drzewiecka-Matuszek, M. Brindell, G. Stochel, *Chem. Rev.* 2005, *105*, 2647–2694.
- [13] a) Y. Zhu, H. Cao, L. Tang, X. Yang, C. Li, *Electrochim. Acta* 2009, 54, 2823–2827; b) J. Li, H. Li, Y. Xue, H. Fang, W. Wang, *Sens. Actuators B* 2014, 191, 619–624.
- [14] a) L. Cui, J. Hu, M. Wang, X.-k. Diao, C.-c. Li, C.-y. Zhang, *Anal. Chem.* **2018**, *90*, 11478–11485; b) K. Lu, C. Hong, D. Liu, Y. He, J. Sun, N. Jia, *Sens. Actuators B* **2022**, *371*, 132588.
- [15] a) L. Guo, Z. Li, K. Marcus, S. Navarro, K. Liang, L. Zhou, P. D. Mani, S. J. Florczyk, K. R. Coffey, N. Orlovskaya, Y.-H. Sohn, Y. Yang, *ACS Sens.* **2017**, *2*, 621–625; b) J. Zhao, C. Fu, C. Huang, S. Zhang, F. Wang, Y. Zhang, L. Zhang, S. Ge, J. Yu, *Chem. Eng. J.* **2021**, *406*, 126892; c) J. Wu, P. Ou, Y. Lin,

Angew. Chem. Int. Ed. 2023, e202311482 (8 of 9)

X. Tan, F. Wei, Y. Mi, S. Liu, K. Huang, J. Electroanal. Chem. **2022**, *911*, 116220.

- [16] C. Wang, Y. Wang, K. O. Kirlikovali, K. Ma, Y. Zhou, P. Li, O. K. Farha, *Adv. Mater.* **2022**, *34*, 2202287.
- [17] M. Mastalerz, Chem. Eur. J. 2012, 18, 10082-10091.
- [18] a) X. Song, Y. Wang, C. Wang, D. Wang, G. Zhuang, K. O. Kirlikovali, P. Li, O. K. Farha, J. Am. Chem. Soc. 2022, 144, 10663–10687; b) Q. Yin, P. Zhao, R.-J. Sa, G.-C. Chen, J. Lü, T.-F. Liu, R. Cao, Angew. Chem. Int. Ed. 2018, 57, 7691–7696; c) B.-T. Liu, S.-H. Gong, X.-T. Jiang, Y. Zhang, R. Wang, Z. Chen, S. Zhang, K. O. Kirlikovali, T.-F. Liu, O. K. Farha, R. Cao, Nat. Synth. 2023, https://doi.org/10.1038/s44160-023-00316-4.
- [19] a) W. Yang, B. Li, H. Wang, O. Alduhaish, K. Alfooty, M. A. Zayed, P. Li, H. D. Arman, B. Chen, *Cryst. Growth Des.* 2015, 15, 2000–2004; b) Q. Yin, J. Lü, H.-F. Li, T.-F. Liu, R. Cao, *Cryst. Growth Des.* 2019, 19, 4157–4161.
- [20] Y. Wang, D. Liu, J. Yin, Y. Shang, J. Du, Z. Kang, R. Wang, Y. Chen, D. Sun, J. Jiang, *Chem. Commun.* **2020**, *56*, 703–706.
- [21] a) X.-T. He, Y.-H. Luo, Z.-Y. Zheng, C. Wang, J.-Y. Wang, D.-L. Hong, L.-H. Zhai, L.-H. Guo, B.-W. Sun, ACS Appl. Nano Mater. 2019, 2, 7719–7727; b) Q. Yin, E. V. Alexandrov, D.-H. Si, Q.-Q. Huang, Z.-B. Fang, Y. Zhang, A.-A. Zhang, W.-K. Qin, Y.-L. Li, T.-F. Liu, D. M. Proserpio, Angew. Chem. Int. Ed. 2022, 61, e202115854.
- [22] X.-T. He, Y.-H. Luo, D.-L. Hong, F.-H. Chen, Z.-Y. Zheng, C. Wang, J.-Y. Wang, C. Chen, B.-W. Sun, ACS Appl. Nano Mater. 2019, 2, 2437–2445.
- [23] a) K. Zeng, Z. Tong, L. Ma, W.-H. Zhu, W. Wu, Y. Xie, *Energy Environ. Sci.* **2020**, *13*, 1617–1657; b) M. Urbani, M. Grätzel, M. K. Nazeeruddin, T. Torres, *Chem. Rev.* **2014**, *114*, 12330–12396.
- [24] a) Y. Wang, K. Ma, J. Bai, T. Xu, W. Han, C. Wang, Z. Chen, K. O. Kirlikovali, P. Li, J. Xiao, O. K. Farha, *Angew. Chem. Int. Ed.* **2022**, *61*, e202115956; b) Y. Suzuki, M. Gutiérrez, S. Tanaka, E. Gomez, N. Tohnai, N. Yasuda, N. Matubayasi, A. Douhal, I. Hisaki, *Chem. Sci.* **2021**, *12*, 9607–9618.
- [25] X. Gao, W. Lu, Y. Wang, X. Song, C. Wang, K. O. Kirlikovali, P. Li, *Sci. China Chem.* **2022**, 65, 2077–2095.
- [26] a) E. J. Kim, R. L. Siegelman, H. Z. H. Jiang, A. C. Forse, J.-H. Lee, J. D. Martell, P. J. Milner, J. M. Falkowski, J. B. Neaton, J. A. Reimer, S. C. Weston, J. R. Long, *Science* **2020**, *369*, 392– 396; b) Y. Xie, B. Chen, *Matter* **2022**, *5*, 2574–2576.
- [27] W. Yang, F. Yang, T.-L. Hu, S. C. King, H. Wang, H. Wu, W. Zhou, J.-R. Li, H. D. Arman, B. Chen, *Cryst. Growth Des.* 2016, *16*, 5831–5835.
- [28] A. Spek, J. Appl. Crystallogr. 2003, 36, 7-13.
- [29] H. Mao, J. Tang, G. S. Day, Y. Peng, H. Wang, X. Xiao, Y. Yang, Y. Jiang, S. Chen, D. M. Halat, A. Lund, X. Lv, W. Zhang, C. Yang, Z. Lin, H.-C. Zhou, A. Pines, Y. Cui, J. A. Reimer, *Sci. Adv.* 2022, *8*, eabo6849.
- [30] a) B. Yu, T. Meng, X. Ding, X. Liu, H. Wang, B. Chen, T. Zheng, W. Li, Q. Zeng, J. Jiang, *Angew. Chem. Int. Ed.* 2022, 61, e202211482; b) J. Nicks, S. A. Boer, N. G. White, J. A. Foster, *Chem. Sci.* 2021, 12, 3322–3327; c) Y.-H. Luo, L. Zhang, W.-X. Fang, S.-H. Ma, H. Dong, S. Su, Z.-Y. Zheng, D.-N. Li, L.-H. Zhai, *Chem. Commun.* 2021, 57, 5901–5904.
- [31] a) A. Ciesielski, A. Cadeddu, C.-A. Palma, A. Gorczyński, V. Patroniak, M. Cecchini, P. Samorì, *Nanoscale* 2011, *3*, 4125–4129; b) V. V. Korolkov, M. Baldoni, K. Watanabe, T. Taniguchi, E. Besley, P. H. Beton, *Nat. Chem.* 2017, *9*, 1191–1197; c) A. Ciesielski, M. El Garah, S. Masiero, P. Samorì, *Small* 2016, *12*, 83–95; d) M. O. Blunt, J. C. Russell, M. d. C. Gimenez-Lopez, N. Taleb, X. Lin, M. Schröder, N. R. Champness, P. H. Beton, *Nat. Chem.* 2011, *3*, 74–78.
- [32] J. A. A. W. Elemans, S. Lei, S. De Feyter, Angew. Chem. Int. Ed. 2009, 48, 7298–7332.





- [33] A. Ciesielski, C.-A. Palma, M. Bonini, P. Samorì, Adv. Mater. 2010, 22, 3506–3520.
- [34] Z.-G. Gu, J. Zhang, Coord. Chem. Rev. 2019, 378, 513–532.
- [35] M. Zhao, Y. Huang, Y. Peng, Z. Huang, Q. Ma, H. Zhang, *Chem. Soc. Rev.* 2018, 47, 6267–6295.
- [36] a) T. Pham, G. Li, E. Bekyarova, M. E. Itkis, A. Mulchandani, ACS Nano 2019, 13, 3196–3205; b) B. Liu, L. Chen, G. Liu,

A. N. Abbas, M. Fathi, C. Zhou, ACS Nano 2014, 8, 5304–5314.

Manuscript received: August 7, 2023 Accepted manuscript online: September 7, 2023 Version of record online:



## **Research Articles**



# **Research Articles**

Hydrogen-Bonded Organic Frameworks

- C. Wang, X. Song, Y. Wang, R. Xu, X. Gao,
- C. Shang, P. Lei, Q. Zeng, Y. Zhou, B. Chen,\* P. Li\* \_\_\_\_\_ e202311482

A Solution-Processable Porphyrin-Based Hydrogen-Bonded Organic Framework for Photoelectrochemical Sensing of Carbon Dioxide



A photosensitive and highly conductive 2D hydrogen-bonded porphyrin framework (FDU-HOF-2) has been constructed with large surface areas, controllable thicknesses, and high area to thickness ratios. A label-free photoelectrochemical (PEC) sensor based on a screen-printing electrode with deposited FDU-HOF-2 was fabricated that exhibits excellent selectivity, extremely low detection limit (2.3 ppm), and long-term working stability (> 30 days) for CO<sub>2</sub>.

## 🍠 ## SPACE RESERVED FOR IMAGE AND LINK

Share your work on social media! *Angewandte Chemie* has added Twitter as a means to promote your article. Twitter is an online microblogging service that enables its users to send and read short messages and media, known as tweets. Please check the pre-written tweet in the galley proofs for accuracy. If you, your team, or institution have a Twitter account, please include its handle @username. Please use hashtags only for the most important keywords, such as #catalysis, #nanoparticles, or #proteindesign. The ToC picture and a link to your article will be added automatically, so the **tweet text must not exceed 250 characters**. This tweet will be posted on the journal's Twitter account (follow us @angew\_chem) upon publication of your article in its final (possibly unpaginated) form. We recommend you to re-tweet it to alert more researchers about your publication, or to point it out to your institution's social media team.

Please check that the ORCID identifiers listed below are correct. We encourage all authors to provide an ORCID identifier for each coauthor. ORCID is a registry that provides researchers with a unique digital identifier. Some funding agencies recommend or even require the inclusion of ORCID IDs in all published articles, and authors should consult their funding agency guidelines for details. Registration is easy and free; for further information, see http://orcid.org/.

Dr. Peng Li http://orcid.org/0000-0002-4273-4577 Prof. Banglin Chen http://orcid.org/0000-0001-8707-8115 Xiyu Song http://orcid.org/0000-0002-0208-8259 Peng Lei Chen Wang http://orcid.org/0000-0003-2303-5647 Yao Wang http://orcid.org/0000-0002-0378-1805 Rui Xu Xiangyu Gao Qingdao Zeng Prof. Cheng Shang Prof. Yaming Zhou