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An ultrafast responsive NO₂ gas sensor based on a hydrogen-bonded organic framework material[†]

Yijie Wang,^a Di Liu,^a Jianbo Yin,^a Yanxue Shang,^a Juan Du,^a Zixi Kang,^b Rongming Wang,^b*^{ab} Yanli Chen, ^b Daofeng Sun^b^{ab} and Jianzhuang Jiang *^{ac}

We report the development of a new type of organic semiconductor gas sensor based on a porphyrin-based hydrogen-bonded organic framework (HOF). Owing to the orderly porous structures, the decoration with rich amino sites and the n-type semiconductor nature, this HOF-based sensor exhibits selective NO₂ sensing performance with ultra-fast response/recovery rates (17.6 s/15.4 s over 100 ppb) and a limit of detection lower than 40 ppb, together with high sensitivity, good reproducibility, and long-term stability at room temperature. This study demonstrates that HOF-based materials have potential application prospects in gas sensing, thereby offering a new way of thinking for the design and development of sensors.

With the development of social economy, efficient detection of various toxic and harmful gases has become very important for production safety and human health protection.¹ Nitrogen dioxide (NO₂), mainly released from motor vehicles and fossil fuel combustion, is one of the most hazardous air pollutants.² It can cause a series of environmental problems, such as acid rain, photochemical smog and ozone layer destruction.³ Long-term inhalation of NO₂ even at several ppm concentrations will also cause serious health problems including headaches, lung inflammation, and eye and throat burns.⁴ According to the World Health Organization guidelines for air quality, the annual and hourly safety limits for the NO₂ concentration at room temperature are approximately 21.9 and 109.6 ppb, respectively. Therefore, it is highly necessary to develop NO₂ sensors with rapid, highly sensitive and selective performance for air-quality monitoring.

As a traditional type of chemiresistor material, metal oxides (MOs), such as SnO₂, ZnO, and Fe₂O₃, have been developed for the detection of various gases including NO₂ owing to their simple fabrication methods, low cost, reversibility and longterm stability of use.^{4,5} However, some disadvantages including poor selectivity, high working temperature and detection limit, as well as slow response to target gases hinder their practical applications. Therefore, tremendous effort has been devoted to develop new materials, such as metal sulfides, nitrogen-doped carbon nanotubes, metal oxides with different morphologies or noble metal decoration, and their composites, in order to address these issues.⁶ Owing to the advantage of operating at room temperature, organic semiconductor sensors are also a promising candidate for the sensing of various gases including NO₂.⁷ Recently, some metal-organic frameworks (MOFs) have been explored to construct highly efficient gas sensors due to their tunable pore size and abundant host-guest interactions. For instance, Xu and co-authors demonstrated that MOFs could significantly improve the gas sensing performance of MOs by forming core-shell structures.8 Mirica and co-authors developed an excellent gas sensor based on two-dimensional (2D) MOF materials.9 In 2019, Zhao and Kim displayed the feasibility of tuning the gas sensing performance by introducing functional groups into MOF channels.¹⁰ However, some issues like complicated sampling processes and slow response to analytes still exist, and no MOF-based NO2 sensors have been reported, as these explorations are still in their early stages. Therefore, it is still urgent to construct gas sensors with a single-step preparation procedure, high sensitivity and rapid response to specific target molecules by rational structural design.

As the counterparts of MOFs, hydrogen-bonding organic frameworks (HOFs), self-assembled by organic building units depending on hydrogen bonds, possess various advantages including orderly pore structures, easy synthesis, and facile renewability and recyclability, and have revealed excellent properties in the fields of gas storage and separation, molecular recognition, catalysis, and proton conduction.¹¹ However, to date, there has been no report about HOF-based gas sensors,

^a College of Science, China University of Petroleum (East China), Qingdao, Shandong 266580, China. E-mail: rmwang@upc.edu.cn

^b State Key Laboratory of Heavy Oil Processing, School of Materials Science and Engineering, China University of Petroleum (East China), Qingdao, Shandong 266580, People's Republic of China

^c Beijing Key Laboratory for Science and Application of Functional Molecular and

Crystalline Materials, Department of Chemistry, University of Science and

Technology Beijing, Beijing 100083, China. E-mail: jianzhuang@ustb.edu.cn

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to the best of our knowledge. In this work, we developed a new type of gas sensor by a single suspension deposit method using a stable porphyrin-based HOF, $H_2TDPP\cdot4DMF\cdot2H_2O$ (UPC-H4a), constructed by a 5,10,15,20-tetrakis(4-(2,4-diaminotriazinyl)phenyl)porphyrin (H_2TDPP). Since UPC-H4a is an n-type semiconductor and contains a large number of free amino groups in ordered channels, this sensor exhibits selective NO₂ sensing performance with high sensitivity, a low limit of detection, ultra-fast response/recovery rates, good repeatability, and longterm stability at room temperature.

An unstable HOF, H₂TDPP·4DMF·2H₂O·2CH₃CH₂OH (UPC-H4), was first prepared by the assembly of H2TDPP under solvothermal condition. Single-crystal X-ray diffraction structural analysis shows that it crystallizes in the monoclinic $P2_1/c$ space group, Table S1 (ESI†). As shown in Fig. 1a–c, the hydrogen-bonded and local π – π interactions between H2TDPP molecules lead to the formation of a three-dimensional (3D) framework with one-dimensional (1D) wide hexagonal channels. UPC-H4a was obtained based on a single-crystal-to-single-crystal (SCSC) transformation by allowing UPC-H4 to stand at room temperature for more than 8 days, which has exactly the same space group and structural features with UPC-H4, only with the loss of lattice ethanol molecules, Fig. 1d. However, the cell parameters show that the framework of UPC-H4 becomes slightly shrunk after losing ethanol molecules, Table S1 and S2 (ESI†).

As shown in Fig. 2a, the powder X-ray diffraction (PXRD) pattern of the freshly-prepared UPC-H4 matches well with the one simulated from its single crystal diffraction data, demonstrating the high phase purity of the as-synthesized samples with the assistance of elemental analysis. However, its PXRD pattern gradually changes when allowed to stand under ambient conditions, and becomes closely consistent with the one simulated from the single crystal diffraction data of UPC-H4a after 8 days, showing the complete loss of lattice ethanol molecules



Fig. 1 (a) The 3D hydrogen-bonded network of UPC-H4; (b) the π - π interactions between the porphyrin structures; (c) the hydrogen-bond modes in UPC-H4; and (d) the 3D hydrogen-bonded network of UPC-H4a.



Fig. 2 (a) PXRD patterns showing the change in the course from UPC-H4 to UPC-H4a under ambient conditions; and (b) the *in situ* PXRD patterns of UPC-H4a.

and formation of UPC-H4a. Similarly, the PXRD test and elemental analysis show that the as-synthesized samples of UPC-H4a also have a high phase purity. However, unlike UPC-H4, UPC-H4a exhibits a good framework stability even after heating to 180 °C and losing all the lattice solvent molecules, Fig. 2b. Correspondingly, TG analysis shows that UPC-H4 slowly loses 28.5% weight from room temperature to 200 °C, which corresponds to the loss of lattice solvent molecules (calculated value 28.6%), and then the framework remains stable until 350 °C and then becomes collapsed slowly after this temperature. In contrast, UPC-H4a loses 23.6% weight until 220 °C, which also corresponds to the loss of lattice solvent molecules (calculated value 23.8%), and the framework also becomes collapsed slowly after 350 °C, Fig. S1 (ESI[†]). The results are in good agreement with the results of the single crystal diffraction and elemental analyses, indicating the high thermal stability of UPC-H4a.

In order to demonstrate the permanent porosity of the UPC-H4a framework, the as-synthesized sample was activated to remove the lattice solvent molecules under vacuum at 160 °C for 24 h, Fig. S2 (ESI†). Then, gas uptake measurements on the desolvated samples were carried out at different temperatures. As expected, UPC-H4a hardly adsorbs N₂ and H₂ even at 77 K because of the hydrophilic nature of the channels based on the existence of a large number of amino groups without forming hydrogen bonds, Fig. S3 and S4 (ESI†). However, it can adsorb 96 cm³ g⁻¹ of CO₂ at 196 K, Fig. S5 (ESI†). The total pore volume calculated from the CO₂ isotherm ($P/P_0 = 0.98$) is 0.20 cm³ g⁻¹, and the Brunauer–Emmett–Teller surface area is 210.5 m² g⁻¹ by fitting the CO₂ isotherm for UPC-H4a, Fig. S6 (ESI†). These results clearly show the permanent porosity and selective adsorption performance of UPC-H4a.

Considering the orderly permanent porosity with the decoration of amino groups, the activated UPC-H4a was coated on the ITO/glass interdigitated electrode by a single suspension deposit method to form a thin film for chemiresistor gas sensing, Fig. S7 (ESI†). In contrast, the sensor based on the activated as-synthesized precursor (H_2 TDPP) was also prepared in the same way. As shown in Fig. S8a–d (ESI†), it can be clearly seen that both UPC-H4a and the precursor evenly cover the surface of the interdigital electrode, but the former exists in the form of regular rod shaped single-crystals, and the latter is a solid with an irregular shape. It should be noticed that although the structure of the precursor is not ordered in comparison with the single crystal structure of UPC-H4a, it is more ordered than that of the completely amorphous powder because the strong hydrogen bonding interactions between H₂TDPP molecules may lead to a relatively directional assembly during the synthesis, Fig. S8e (ESI†).

To demonstrate the application potential of the aforementioned devices, electron conductivity measurements were first performed in dry nitrogen (RH = 0%), and the currentvoltage (I-V) characteristics for UPC-H4a and the precursor are shown in Fig. S9 (ESI⁺). For the accuracy of the results, this and the following experiments were conducted for more than three different devices and at least three times on each sample. Two materials exhibit obviously different conductive behavior, with a conductivity (σ) of about 1.2 \times 10⁻⁴ S cm⁻¹ and 6.8×10^{-6} S cm⁻¹ for UPC-H4a and the precursor, respectively. The higher conductivity of UPC-H4a might be caused by the stronger π - π interactions among the adjacent porphyrin molecules in the more orderly structure as observed in the single crystal structure, Fig. 1b. This is also demonstrated by the spectral characterization of UPC-H4a and the precursor. Compared with the UV-vis spectrum of the precursor, the Soret bands of porphyrin for UPC-H4a not only show a significant red-shift from 415 nm to 433 nm, but also adopt a broader shape with a lower peak strength, indicating the formation of a J-aggregation type in UPC-H4a, Fig. S10 (ESI⁺). Similarly, the intense emission band (655 nm) of the fluorescence spectrum of UPC-H4a also displays a red-shift relative to the one (652 nm) of the precursor, further demonstrating the formation of better J-aggregation in UPC-H4a, Fig. S11 (ESI†). When compared with the IR spectrum of the precursor, the one of UPC-H4a shows broader N-H stretching vibration shapes at 3311 and 3173 cm⁻¹, suggesting the formation of more N-H···N hydrogen bonds in UPC-H4a, Fig. S12 (ESI⁺). Meanwhile, the N-H in-plane bending vibrations in UPC-H4a also shift to 1664 cm⁻¹ from 1656 cm⁻¹ in the precursor, and have an obvious strength enhancement, revealing stronger π - π interactions among the pyrrole rings of porphyrins. These results clearly disclose that the formation of HOFs can regulate the intermolecular stacking modes and in turn affect the electron conductivity of the materials.

The gas sensing performance of these two sensors was evaluated using different concentrations of target gases (H₂S, CO_2 , NH_3 , H_2 , SO_2 or NO_2) in N_2 at room temperature. As shown in Fig. 3a and Fig. S13a (ESI[†]), negative current responses are observed upon exposure of two sensor devices to NO2 (40-2000 ppb) under a bias of 5 V, demonstrating the n-type conductivity nature of UPC-H4a and the precursor.7b The percent current variation is calculated as responsivity (R%) to evaluate the effect of NO2 on responses, which is defined as $R\% = (I_{\rm off} - I_{\rm on})/I_{\rm off} \times 100\%$, where $I_{\rm off}$ is the current at the start of an exposure/recovery period and $I_{\rm on}$ is the current at the end of the exposure period. For the UPC-H4a sensor, the R% values to 100, 500, 1000, and 2000 ppb are 6.9%, 20.1%, 32.7%, and 43.3%, respectively. For the precursor sensor, the R% values to 100, 500, 1000, and 2000 ppb NO₂ amount to only 2.2%, 8.2%, 12.7%, and 15.0%, respectively. Correspondingly, the



Fig. 3 (a) The response-recovery curve of the UPC-H4a sensor toward different concentrations of NO₂ at room temperature; (b) the linear relation between R° and the concentration; (c) response-recovery time curves to 100 ppb NO₂; and (d) responsivity and sensitivity to 1 ppm different gases.

sensitivities (% ppm^{-1}), defined as the slope of linear correlation between responsivity and the NO2 concentration, are 29.3% and 10.1% for the UPC-H4a and precursor sensors, respectively, Fig. 3b and Fig. S13b (ESI⁺). Considering that the limit of detection (LOD) is a key parameter in gas sensing, a lower concentration of NO2 is used to explore the LOD of the two sensors. It can be clearly seen that the UPC-H4a sensor exhibits an excellent response to NO2 with an easily detected R% value of 4.2%, even at a very low concentration of 40 ppb limited by our gas mixture system. This means that the UPC-H4a sensor has a limit of detection (LOD) lower than 40 ppb, which is lower than the annual safety limits (109.6 ppb) of the NO₂ concentration stipulated by the World Health Organization. In fact, it could also be lower than the stipulated hourly safety limits (21.9 ppb) because the R% is still an easily detected value (4.1) when extending the sensitivity fitting curve obtained from the range of 40-1000 ppb to 20 ppb.12 In contrast, no obvious response was observed when the concentration of NO2 was smaller than 100 ppb for the precursor sensor, revealing that its LOD is almost 100 ppb. These results demonstrate that the UPC-H4a sensor possesses higher sensitivity and a lower LOD than the precursor owing to the better conductivity performance and the more number of -NH2 active sites interacting with NO2 related to its orderly pore structure as mentioned above.

According to the above results, the response/recovery times as the important parameters of the sensors were also studied. In this work, the response time ($T_{\rm res}$) was defined as the time taken for decreasing the starting current to 10% when exposed to NO₂, and the recovery time ($T_{\rm rec}$) was defined as the time taken for increasing the current to 90% of the starting current when exposed to pure N₂. As shown in Fig. S13c (ESI†), the precursor sensor exposed to 100 ppb NO₂ shows $T_{\rm res}$ and $T_{\rm rec}$ values of 24.8 and 46.8 s, respectively. However, the $T_{\rm res}$ and $T_{\rm rec}$ values of the UPC-H4a sensor exposed to 100 ppb NO₂ are significantly shortened to 17.6 and 15.4 s, respectively, due to the fast diffusion of NO₂ in the ordered channels of the latter material, Fig. 3c. The detailed data are listed in Table S3 (ESI†). These results reveal that the UPC-H4a sensor exhibits ultrafast response/recovery rates to NO_2 at room temperature, because the ordered pore structure is conducive to the rapid diffusion of NO_2 , and the hydrophilic $-NH_2$ has a rapid enrichment effect on NO_2 .

Towards the practical application of gas sensors, selectivity and reproducibility are two factors that must be considered. Owing to the hydrophilic feature of UPC-H4a channels, the competitive gases including SO₂, H₂S, CO₂ and NH₃ as well as H₂ were selected to investigate the sensing selectivity of the two sensors to NO₂. As shown in Fig. 3d and Fig. S13d, S14-S18 (ESI⁺), both UPC-H4a and precursor sensors show no obvious sensing performance for these five gases, indicating that the UPC-H4a sensor exhibits excellent selective sensing towards NO2. The selective sensing mechanism can be interpreted by an adsorption-oxidation-desorption process.4 The XPS spectra clearly show that the activated UPC-H4a can absorb O₂ and transfer electrons to O_2 to form chemisorbed O_2^- and O^- (532.3 eV) after exposure to air due to the nature of the electron-rich n-type semiconductor, Fig. S19 (ESI⁺). When it is further exposed to oxidizing NO₂, the NO₂ can enter its hydrophilic channels and directly capture electrons (NO₂ + $e^- \rightarrow$ NO_2^{-}) or react with the chemisorbed O_2^{-} ($NO_2 + O_2^{-} + 2e^{-} \rightarrow e^{-}$ $NO_2^- + 2O^-$) to form NO_2^- and O^- . The decrease of the electron concentration in UPC-H4a leads to a resistance increase of the sensor, Fig. 3a and Fig. S13a (ESI⁺). After the sensor is exposed to air or nitrogen again, NO2⁻ releases the captured electrons back to UPC-H4a and desorbs, resulting in the resistance recovery of the sensor. However, the reductive and weakly oxidizing gases cannot capture electrons from UPC-H4a to cause changes in resistance. In addition, ten successive response/ recovery cycles were performed on the two sensors toward 1 ppm and 100 ppb NO₂, respectively, at room temperature. It can clearly be seen that the response/recovery curves remain consistent during cycling, Fig. S20a and S21a (ESI⁺). In order to study the long-term stability of the sensors, the response/recovery curves to NO2 were also tested every 10 days in a 60 day period. Similarly, no significant change in the sensing performance is observed after 60 days, Fig. S20b and S21b (ESI⁺). The structure stability of UPC-H4a was also confirmed by the PXRD pattern, which was obtained through immersing its crystals into 1 ppm NO₂ for 30 min, Fig. S22 (ESI⁺). These results show that the UPC-H4a sensor bears excellent reproducibility and long-term stability for NO2 sensing.

In summary, a new type of organic semiconductor gas sensor was constructed by a single suspension deposit method based on a stable porous porphyrin-based HOF material, which was obtained through SCSC transformation from an unstable HOF. The ordered distribution of free amino groups along the 1D channels of UPC-H4a enables this HOF-based sensor to exhibit excellent selectivity and ultrafast response toward NO₂ with a low limit of detection at room temperature. Moreover, this novel HOF-based sensor also displays good reproducibility and long-term stability. These results not only demonstrate the application potential of HOF-based sensors but also provide a new way of thinking for the design and development of sensors with high selectivity and low limit of detection. Future work will be devoted to studying the gas sensing performance of the sensor with *in situ* growth of HOF films.

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Conflicts of interest

There are no conflicts to declare.

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