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**Solution-Processed Nanoporous Organic Semiconductor Thin Films:
Towards Health and Environmental Monitoring of Volatile Markers**

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Abstract

Porous materials are ubiquitous in nature and have found a wide range of applications owing to their unique absorption, optical, mechanical and catalytic properties. Large surface-area-to-volume ratio is deemed a key factor contributing to their catalytic properties. Here we show that introducing tunable nanopores (50 – 700 nm) to organic semiconductor (OSC) thin films enhances their reactivity with volatile organic compounds by up to an order of magnitude, while the surface-area-to-volume ratio is almost unchanged. Mechanistic investigations inform that nanopores grant direct access to the highly reactive sites otherwise buried in the conductive channel of the transistor. The high reactivity of nanoporous organic

field-effect transistors leads to unprecedented ultrasensitive, ultrafast, selective chemical sensing below 1 ppb level at hundred-millisecond time scale, enabling a wide range of health and environmental applications. We further demonstrate flexible sensor chip for monitoring breath ammonia – a potential biomarker for chronic kidney disease.

1. Introduction

Organic semiconductors (OSC) have emerged as a new class of electronic materials promising a wide range of applications from organic field-effect transistors (OFET), solar cells, thermoelectrics, electronic skins, chemical and mechanical sensors by virtue of their chemical versatility, solution processability and mechanical flexibility.^[1-11] Controlled fabrication of nanoporous OSCs over large area can open up a new avenue to tune the (opto)electronic properties, and may even lead to new functions not imagined before, given the wide utility of nanoporous materials for energy storage, chemical separation, catalysis, drug delivery and beyond. Recent work by Cho and Oh et al. has elegantly demonstrated the fabrication of large-domain porous pentacene thin films by vapor deposition on a small molecule template.^[3] Follow-up works have also shown fabrication of porous OSC thin films exhibiting enhanced gas sensing performance.^[12-14] However, solution coated/printed nanoporous OSCs has not been reported before. In addition, the methods demonstrated thus far are not material-agnostic and do not offer wide tunability of pore sizes. Pore structure

tunability is particularly important for controlling the pore-imparted properties, such as sensitivity and response time of OFET based chemical sensors.

In this work, we demonstrate a generic method to fabricate nanoporous thin films, applicable to both polymer and small molecule OSCs. We introduce nanopores with tunable pore sizes (50 – 700 nm) into the semiconductor thin film via simple solution processing methods such as meniscus-guided coating/printing and spin-coating. We further fabricate nanoporous OFET sensors for detection of volatile organic compounds (VOCs) such as ammonia and formaldehyde. Sensitive and rapid VOC detection using printed low-cost sensor chips has potential applications in personalized health and environmental monitoring.^[15-16] However, it remains a challenge for OFET-based sensors to attain the high sensitivity (ppb level), fast response (sub-second) and resilience to confounding factors (moisture, temperature) required for these applications. We show that introducing nanopores to OFET sensors enhanced the response at low concentration and reduced the response time to VOCs, while retaining the resilience to confounding factors. Furthermore, thanks to tunable pore dimensions, we are able to investigate pore-size dependent sensing performance and establish a reaction-diffusion model to elucidate nanopore-enhanced sensing mechanism. Our proposed mechanism is against the conventional wisdom that attributes enhanced sensing performance to high specific surface area and/or enhanced diffusion.^[3, 13, 17-20] The high sensing performance obtained using our method could further enable potential applications in breath sensing and environmental monitoring.

2. Results and Discussion

2.1. Templating nanoporous OSC thin films

We demonstrate a simple, additive approach to fabricate nanoporous semiconductor thin films in solution processing. The solution processing methods we used include spin coating and meniscus-guided unidirectional coating; the latter shares the same fundamental physics as large-scale roll-to-roll printing (**Figure 1a**). The simplicity and generality of this approach for fabricating nanoporous thin films stand in contrast to the conventional subtractive approaches based on lithography and etching, which involve complex procedures and corrosive chemicals.^[21-23]

The key to our method is to direct the semiconductor deposition using a nanoporous insulating layer serving as the template, which can be fabricated over a large area via one-step microphase separation during spin coating. The nanoporous template was prepared from poly(4-vinylphenol) (PVP) /tetrahydrofuran (THF) solution with 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (HDA) added as the cross-linking agent for PVP (**Figure S1**). Nanopores ranging from 50 nm to 700 nm in pore diameters were obtained by systematically increasing the HDA:PVP ratio in the solution (**Figure 1b-e** and **Figure S2a**). Through Hansen solubility parameter^[24-25] calculations (**Table S1**), we infer that addition of HDA decreases the miscibility of PVP with THF, which was experimentally validated by the miscibility test (**Figure S3**). Furthermore, AFM characterizations revealed that the nanopores extend through the entire thickness of the PVP:HDA film (**Figure S2b**). Combining the miscibility test with morphology characterizations of the nanoporous thin film, we hypothesize that elevated HDA concentration induces microphase separation in-

plane, between a continuous PVP-rich phase and a discrete THF-rich phase by the mechanism of nucleation and growth. Subsequent THF evaporation leaves nanopores in the film. We further propose that increasing HDA concentration expedited THF domain nucleation, thereby prolonging domain growth to result in larger pore formation (Supplementary Note 1 and Figure S4).

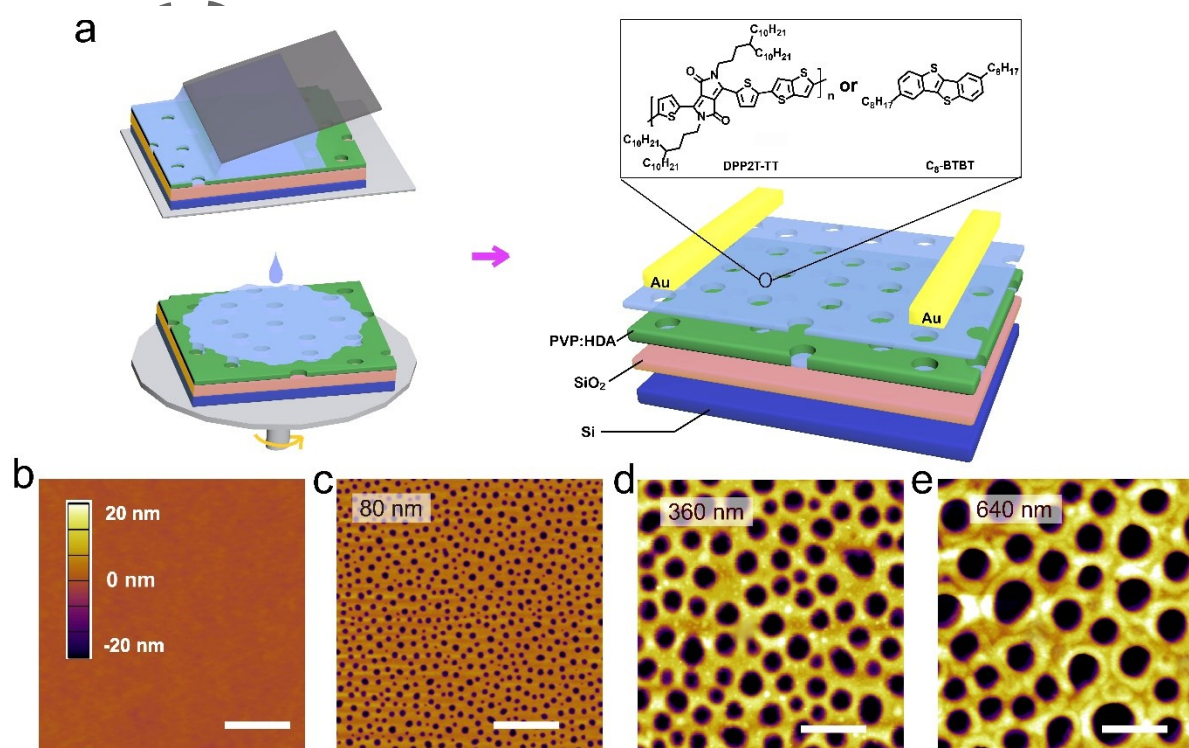


Figure 1. Nanoporous semiconductor thin film fabrication via simple solution processing. (a) Schematic of nanoporous semiconductor layer formation templated by a nanoporous PVP:HDA layer via meniscus-guided coating and spin-coating. Also shown is the corresponding nanoporous field-effect transistor device with DPP2T-TT or C₈-BTBT as the active layer, SiO₂ as the dielectric layer and doped Si as the gate electrode. (b-e) Atomic Force Microscopy (AFM) height images of porous PVP:HDA templates, with average pore diameter of (b) 0 nm (c) 80 nm, (d) 360 nm, (e) 640 nm. The scale bars are 1 μm in all images.

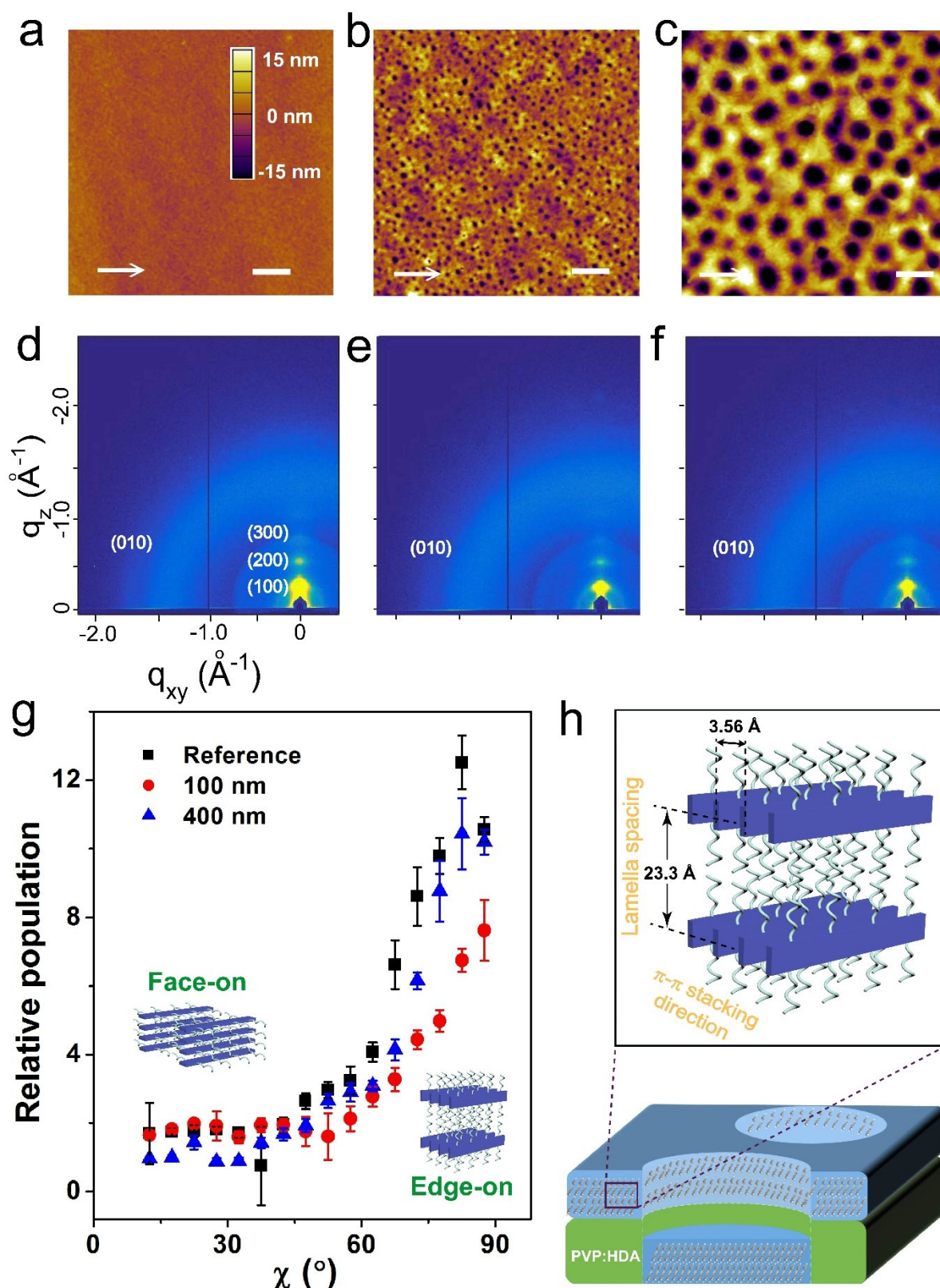
With the nanoporous PVP:HDA template prepared, we next deposited organic semiconductor thin film on the template layer using either spin-coating or meniscus-guided

coating (Figure 1a). We first deposited poly(diketopyrrolopyrrole-thiophene-thieno[3,2,b]thiophene-thiophene) (DPP2T-TT), a recently reported high performance donor-acceptor conjugated polymer.^[26-28] Before deposition, we grafted a monolayer of octadecyl trichlorosilane (OTS) on the template layer to passivate the charge traps.^[29] After DPP2T-TT deposition, we observed a faithful pattern transfer from the template layer (Figure 1b-e) to the semiconductor layer (**Figure 2a-c** and **Figure S5a-c**) using both solution processing methods. The DPP2T-TT polymer formed a continuous thin film with isolated nanopores decorating the entire surface. The continuity of the thin film is important for providing percolation pathways for the charge carriers in a transistor device. From AFM height images, we measured that the pore diameter and pore depth in the semiconductor layer remain almost the same as those in the template layer, across the entire range of pore sizes tested (**Table S2**). From unchanged pore depth, we infer that the template pore floors are coated with DPP2T-TT of the same thickness as that on the top surface. The almost identical pore diameter before and after DPP2T-TT deposition indicates that the pore walls are not coated by the polymer film, particularly considering that the DPP2T-TT film thickness is by no means negligible (~23 nm). We later show that this morphology feature is important for enhancing chemical response by exposing the conductive channel of the transistor device.

We further characterized the molecular packing in the nanoporous semiconductor films by Grazing-incidence X-ray diffraction (GIXD) (Figure 2d-f, Figures S5 and S6). The detailed molecular packing analysis is summarized in Supplementary **Table S3** and **Table S4**. Not surprisingly, the presence of nanopores did not noticeably alter the molecular packing in the DPP2T-TT thin film. Figure 2g shows the geometrically corrected orientation distribution of

crystallites in coated DPP2T-TT films obtained from pole-figure analysis on the π - π stacking ring.^[30-33] The analysis unveiled a predominant edge-on orientation of the π stacks (Figure 2h) in all cases tested regardless of the processing methods and the pore sizes. We expect this preferred orientation to promote the charge-transfer reaction with the analyte by maximizing the exposure of the π orbitals of the conjugated core at the pore wall.

How does the nanoporous template direct the semiconductor deposition process to yield the observed morphology? First, we determined that the polymer ink solution is in the Wenzel state when in contact with the nanoporous template (**Figure S7**), indicating that the ink wets the entire contour of the template layer. Therefore, we expect the polymer deposition on the pore floor to occur in the same fashion as on the top surface, both driven by solvent evaporation at the triple-phase contact line. When the meniscus sweeps over the vertical pore wall, however, deposition does not have time to occur due to the constant meniscus speed along the coating direction. The consistently low contact angle between the ink and the entire porous template may have also prevented contact line pinning and therefore no deposition occurred at the pore wall (**Figure S8**). The same mechanism applies to the deposition of 2,7-dioctyl [1]benzothieno[3,2-b]benzothiophene (C₈-BTBT), a small molecule semiconductor as shown later.



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Figure 2. Morphology Characteristics of printed DPP2T-TT thin films. (a-c) AFM images and (d-f) GIXD diffraction patterns of printed DPP2T-TT film on the PVP:HDA template layer with pore size of (a, d) 0 nm, (b, e) 100 nm and (c, f) 400 nm. The scale bars are 1 μ m in all AFM images. Films were printed at 0.5 mm/s from 3 mg/mL chloroform solution at room temperature. Arrows indicate the printing direction. GIXD was taken with the printing direction is parallel to the incident beam (shown here) as well as perpendicular to the incident beam (Figure S6). The GIXD images are not geometrically corrected to show the lamella peaks clearly. (g) Comparison of geometrically corrected orientation distribution for printed DPP2T-TT film with various pore sizes. The plot at polar angle $\chi = 0^\circ$ indicates face-on orientation and $\chi = 90^\circ$ represents edge-on orientation. The normalized diffraction intensities scale with the population of the crystallites with orientation characterized by the polar angle χ . The error bars were standard errors of calculated (010) peaks areas from multipeak fitting. (h) Schematic illustrating the cross-sectional morphology of porous DPP2T-TT film (blue) printed on the porous PVP:HDA template (green). The magnified image shows the edge-on molecular packing in the DPP2T-TT layer.

2.2. Nanoporous polymer OFET for ammonia sensing

To characterize the charge transport properties and sensing performance of the nanoporous semiconductor thin films, we fabricated top contact bottom gate transistor devices and performed electrical measurements under ambient conditions (**Figure 3**). Typical transfer curves of DPP2T-TT OFETs with and without pores are shown in Figure 3a. Both devices exhibited predominant hole transport with an on/off ratio of $\sim 10^5$. The DPP2T-TT based nanoporous OFETs had comparable mobility ($0.30 \pm 0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) but slightly lower on-current compared to the nonporous devices, due to a slight decrease in capacitance when the nanostructured template layer was introduced (**Figure S9**). This observation confirms that introducing nanopores did not adversely influence the device performance. Notably, the transistor devices remained stable after repeated measurements in air, which is ideal for sensing applications (**Figure S10**).

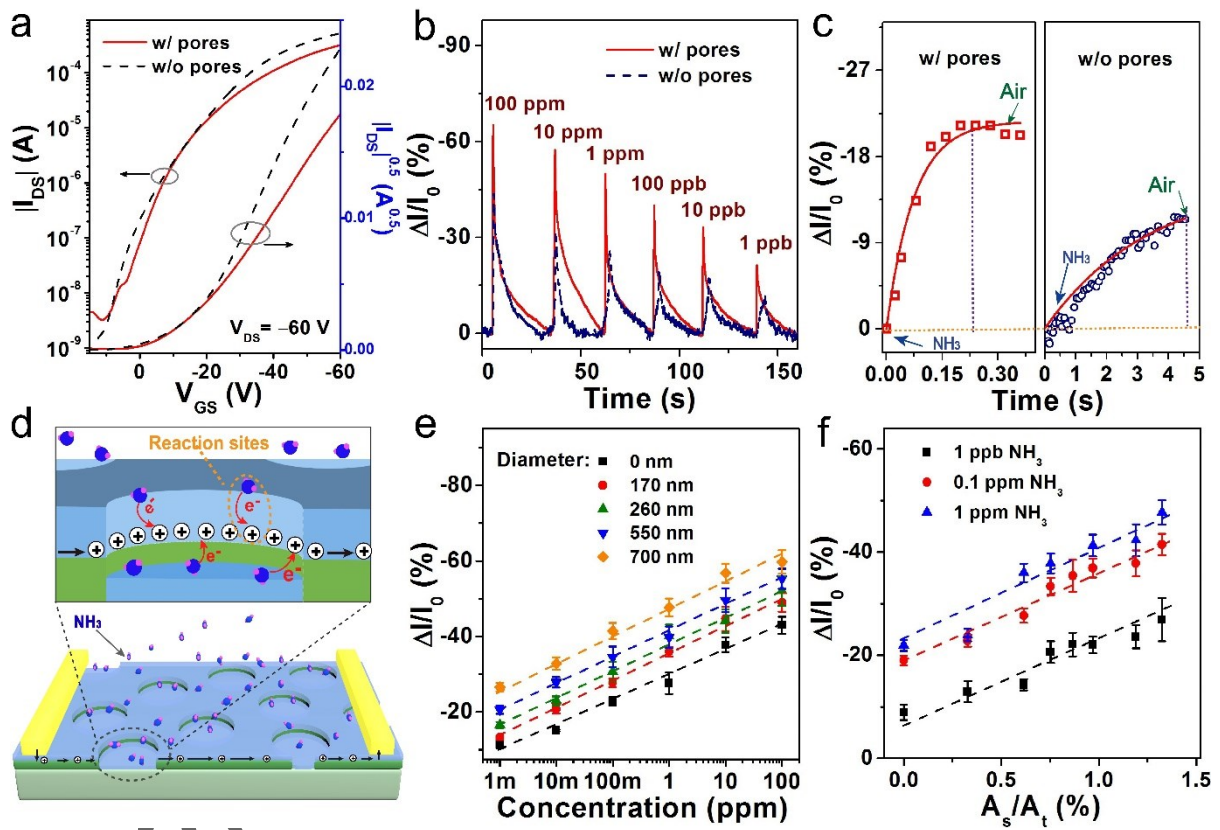


Figure 3 Nanoporous OFET based ammonia sensor. (a) Comparison of transfer curves from porous vs. nonporous OFET. The devices were fabricated with a channel length of $65 \mu m$ and width of $4500 \mu m$. (b) Current responses of DPP2T-TT based sensing device to a series of ammonia gas concentrations at constant voltage ($V_{GS} = -10V$, $V_{DS} = -20V$). The current response ($\Delta I/I_0$) is reflected by the percent change in current ΔI with respect to the initial current I_0 . The devices were fabricated with DPP2T-TT film without (w/o) or with (w/) pores (with a diameter of $\sim 700 nm$). (c) Read-out signals showing percentage current change as a function of time responding to 1 ppb NH_3 . The red lines show the simulated response based on the reaction model. (d) Schematic diagram of the nanoporous OFET-based ammonia sensor. The magnified cartoon illustrates the charge transport reaction occurring at the conductive channel with ammonia. (e) Current response of DPP2T-TT devices to ammonia with concentrations ranging from 1 ppb to 100 ppm. Dependence of $\Delta I/I_0$ on pore sizes is shown. (f) Dependence of $\Delta I/I_0$ on the area fraction of the exposed pore wall. A_s is the total surface area of the pore wall calculated from the film thickness, pore diameter and pore area density. A_t is the total surface area of the semiconductor layer. Error bars were calculated from 6-8 measurements on 3-4 independent samples at each condition.

We next measured the sensing performance of DPP2T-TT transistor to NH_3 in real time.

To this end, the gas sensing experiments were performed in a PDMS microfluidic system that

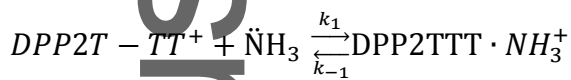
enclosed the transistor devices. When NH_3 molecules are carried into the PDMS channel, they diffuse into the conductive channel of the transistor device and donate electrons to DPP2T-TT via a charge transfer reaction, thereby reducing the hole concentration and resulting in a decrease in the current. The device response to the analyte is presented as $\Delta I/I_0 = (I_g - I_0)/I_0$, where I_0 and I_g denote the initial drain current and the current after exposure to the analyte respectively, and ΔI is the net current change. Figure 3b show the dynamic sensing performance of DPP2T-TT based sensor for detecting NH_3 ranging from 1 ppb to 100 ppm in dry air. Importantly, at the low concentration of 1 ppb, the presence of 700 nm nanopores enhanced the $\Delta I/I_0$ by up to 2.5 times to 27.8% and reduced the response time by an order of magnitude from seconds to hundred milli-second time scale (Figure 3c and **Figure S11**). In comparison, previously reported detection limit is frequently in the hundred ppb range with response time on the order of seconds to minutes (**Table S5**).^[10, 12, 19, 34-35] We note that the lowest gas concentration used in this study is not equivalent to the detection limit. The detection limit can be extrapolated from the linear calibration curve when the signal equals three times the root-mean-square (rms) deviation of the noise level.^[36] The noise level in our system is $< 0.12\%$ in terms of the rms deviation from the $\Delta I/I_0$ baseline, while the signal at 1 ppb gas concentration is two orders of magnitude higher than the noise level. Therefore, the detection limit of our nanoporous sensors will be significantly lower than 1ppb. Our low detection limit, sensitive and ultrafast response are unprecedented among OFET-based NH_3 sensors. The ultrasensitive and ultrafast sensing performance can enable even the most demanding health and environmental applications as demonstrated later.

2.3. Sensing mechanism and reaction model

What is the mechanism by which nanopores promote sensitive response and shorten the response time? We hypothesize that introducing through-pores in the thin film exposes the highly reactive sites originally buried in the conducting channel to the pore wall (Figure 3d). Their high reactivity comes from two aspects: first, the DPP2T-TT molecules in the conducting channel are positively charged serving as hole carriers; second, the backbone of DPP2T-TT is oriented edge-on with respect to the substrate (Figure 2h), thereby favorably exposing the π -electrons to the pore wall. Both factors are expected to promote charge transfer reactions between NH_3 and DPP2T-TT at the pore wall. To test our hypothesis, we systematically varied the pore size and correspondingly the area fraction of the pore wall out of the total surface area (A_s/A_t), and measured the pore-size dependent sensing performance (Figure 3e). We observed that $\Delta I/I_0$ of the device was linearly proportional to the pore wall area fraction A_s/A_t (Figure 3f). This observation is consistent with our hypothesis since the area density of highly reactive sites scales with the area fraction of the conductive channel exposed to the pore wall and therefore A_s/A_t . We further verified that the sensing performance was insensitive to the through-pore thickness when varied between 50 nm to 12 nm (**Figure S12**), but further reducing the thickness to 8 nm started to decrease the response. This result suggests that the conducting channel likely has a thickness between 8-12 nm within which the highly reactive sites reside.

To quantify the extent to which the charge transfer reaction rate is modulated by nanopores, we established a simple analytical model detailed in Supplementary **Note 2** and

Figure S13. One important assumption of the model is negligible diffusional resistance in a low Damköhler number (D_a) regime. This assumption is justified since the estimated diffusion time scale is 10^{-4} s in nanoscopic thin films, which is at least three orders of magnitude shorter than the response time. Therefore, the response time is determined by the charge-transfer reaction alone. Considering a first-order charge-transfer reaction between the hole carrier (DPP2T- TT^+) and the analyte (NH_3), as described by the following first-order reaction:



we derived that device response follows the equation below:

$$\Delta I/I_0 = \frac{1}{1 + \frac{k_{-1}}{k_1 C_{NH_3}}} (1 - e^{-(k_1 C_{NH_3} + k_{-1})t}) \quad \text{Equation 1}$$

where C_{NH_3} represents the concentration of NH_3 , k_1 and k_{-1} are the forward and backward reaction rate constant respectively, and t is the reaction time. It is evident that the sensing performance is highly dependent on the reaction rate constants.

To compare the reaction kinetics for sensors with and without nanopores, we fitted Equation 1 to the experimentally obtained dynamic monitoring curves and regressed the forward and backward reaction rate constants as a function of pore size and A_s/A_t (Figure 3f and **Table S6**). We found that k_1 was enhanced by an order of magnitude when the pore size increased from 0 to 720 nm and correspondingly A_s/A_t increased from 0 to ~1.2%. On the other hand, k_{-1} was not much affected, exhibiting a moderate two-fold increase. This result is

consistent with our hypothesis that nanopores enhances the reactivity of the semiconductor layer by exposing highly reactive sites to the pore wall, resulting in ultrasensitive and ultrafast sensing performance of nanoporous devices. (Figure 3d and Figure S13). It is worth noting that recent studies on OFET gas sensors have reported improved current response by decreasing the film thickness. The observed enhancement was frequently attributed to lowered analyte diffusion barrier.^[19, 35, 37] Our work indicates that enhanced reactivity is key to attaining sensitive response for the device, not removing diffusion barriers in the case of thin film transistor based gas sensors. We emphasize that introducing nanopores dramatically enhanced reactivity with only negligible increase in the specific surface area. This observation is in stark contrast to the mechanism proposed in previous studies on nanostructured OFET sensors.^[13, 17, 20] We believe the highly anisotropic nature of the transistor thin film in terms of both molecular orientations and electronic states is the fundamental reason why nanopores are so effective in enhancing the reactivity towards analyte without substantially increasing the specific surface area. We note that the devices fabricated via meniscus-guided coating and spin coating methods yielded almost the same sensing performance, showing the robustness of our nanoporous approach for attaining high sensing performance (**Figure S14**).

2.4. Nanoporous small molecule OFET for formaldehyde sensing

To demonstrate the generality of our approach, we fabricated nanoporous OFET sensors using a small molecule semiconductor C₈-BTBT via both meniscus-guided coating and spin coating following a similar procedure (see Experimental section). Strikingly, we obtained

large yet nanoporous single-crystalline domains with well-defined terraces (**Figure 4a**). The structural integrity of these large crystalline domains was not affected by introducing a high area density of nanopores. The high crystallinity is manifested in the formation of micron-sized nanoporous terraces of 2.6 nm~2.8 nm in height, indicating that the terraces are comprised of a single molecular layer of C₈-BTBT.^[38] The high crystallinity is also evident from the appearance of high index peaks in the GIXD patterns (**Figure S15**). In addition, only a few Bragg rods were observed due to the large size of crystalline domains well beyond the X-ray beam width, and therefore only very few grains were sampled by the X-ray. Interestingly, coating on nanoporous templates resulted in narrower diffraction peaks compared to the case of nonporous substrate (Figure S15 and **Table S7**). Correspondingly, we measured higher hole mobility in the nanoporous transistor devices (**Table S8**). The mechanism by which nanopores improve molecular ordering in C₈-BTBT thin film is unclear. Nonetheless, high charge carrier mobilities obtained verify the continuity and charge percolation in the nanoporous thin films despite high pore densities.

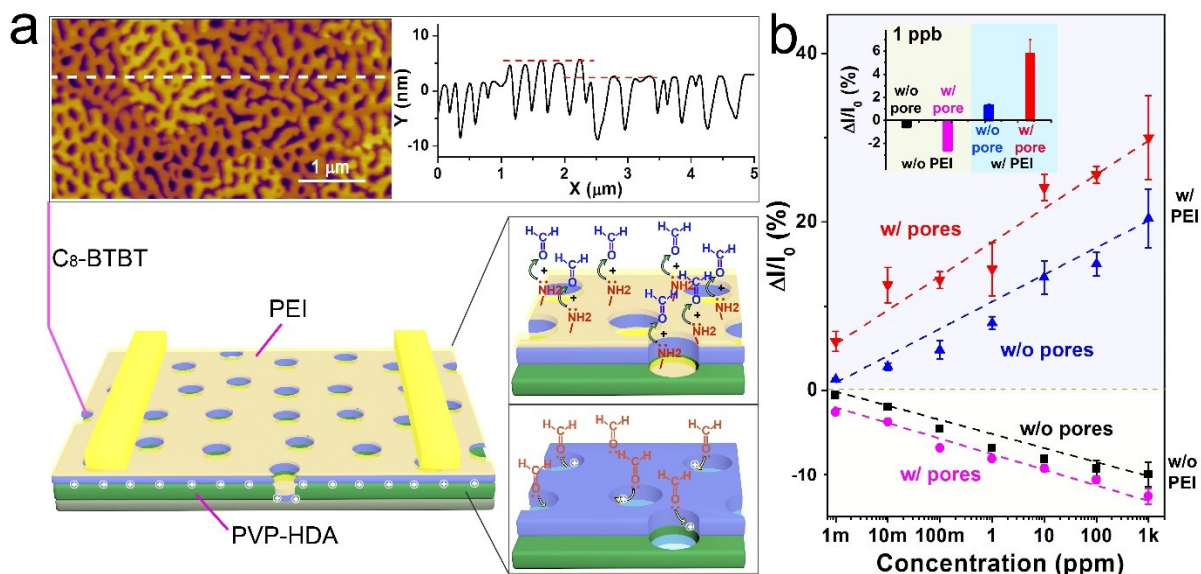


Figure 4. Nanoporous C₈-BTBT OFET sensor. (a) Schematic of the device configuration. The top-contact, bottom-gate transistor device has a nanoporous semiconductor layer templated by the porous PVP:HDA layer, and covered by the PEI sensory layer. The AFM image and cross-sectional profile of the nanoporous C₈-BTBT semiconductor layer are shown. How formaldehyde molecules interact with the device is further illustrated. (b) Current response of C₈-BTBT/PEI transistor device with (red) and without (blue) pores as compared to C₈-BTBT transistor device with (magenta) and without (black) pores to a wide range of formaldehyde gas concentration ($V_{GS} = -40V$, $V_{DS} = -40V$). The inset shows the magnified current responses at 1 ppb formaldehyde concentration. The nanopore size was approximately 500 nm on average.

We next tested the sensing performance of C₈-BTBT OFET for trace formaldehyde detection. Formaldehyde sensing is important and relevant for both environmental and health monitoring. Formaldehyde is a common carcinogenic indoor air pollutant with a recommended long-term exposure of only 16 ppb.^[39-40] In addition, formaldehyde in human breath is a biomarker for breast cancer. A breath formaldehyde concentration exceeding 1.2 ppm is strongly correlated with the disease condition, compared to the healthy level of 0.3 ppm on average.^[41] However, it remains challenging to detect formaldehyde (CH₂O) at such low concentration due to its weak electron donating and withdrawing abilities and therefore

low reactivity with most organic semiconductors^[17, 42], including C₈-BTBT (squares in Figure 4b). Hence, we added a sensory layer to the C₈-BTBT OFET comprised of polyethyleneimine (PEI) rich in primary amine groups to enhance reactivity with CH₂O (Figure 4a). The nanoporous structure was maintained after PEI coating atop the C₈-BTBT layer (**Figure S16**). The as fabricated nanoporous C₈-BTBT/PEI OFET exhibited excellent CH₂O sensing performance in air reaching an unprecedented detection limit below 1 ppb. In particular, introducing nanopores increased the $\Delta I/I_0$ of nonporous devices by an order of magnitude from 0.6% to 5.8%. Without PEI, nanopores also enhanced the current change for device, but to a lesser extent (Figure 4b). From the opposite current responses of devices with vs. without PEI, we infer a doping-dedoping sensing mechanism as the following (Supplementary **Note 3** and **Table S9**). First, PEI acts as an electron donor doping the hole-conducting C₈-BTBT, which brings a decrease in current; when the carbonyl groups of CH₂O reacts with the amine groups of PEI, the C₈-BTBT layer is dedoped and the current rises back. The PEI layer enhances the reactivity with CH₂O while nanopores expose the reactive conducting channel originally buried in the C₈-BTBT layer. Both factors combined leads to the ultrasensitivity and fast response time for CH₂O sensing (**Figure S17**). As far as we know, this is the best sensing performance among OFET-based formaldehyde sensors reported so far. Previous studies typically reported detection limits between 1 ppm to 1000 ppm.^[17] We further show that the nanoporous C₈-BTBT sensors exhibit good selectivity for CH₂O among major reactive VOCs (**Figure S18**), enabling potential applications in ultrasensitive environmental and health monitoring.

2.5. Flexible nanoporous OFETs for breath sensing

The ultralow detection limit and ultrafast response of nanoporous OFET sensors open avenues for a wide range of applications in health and environmental monitoring. In particular, sensing concentration change of breath VOCs could serve as a powerful and low-cost platform for personalized health monitoring and disease prevention by alerting individuals potential onset of a disease condition at a very early stage.^[43-44] Here, we demonstrate low-voltage DPP2T-TT OFET sensor chip fabricated on flexible substrate and its application in sensing breath ammonia (**Figure 5**). Ammonia is a common volatile organic compound found in human breath, which was identified as a key biomarker for end-stage renal failure. Previous studies observed significantly increased breath ammonia concentration at the diseased stage, rising from hundred ppb (healthy) to ppm level (diseased) on average (**Table S10**).^[45-48] Elevated level of ammonia was also found in exhaled breath of patients suffering from liver failure and Alzheimer's.^[16, 49]

To fabricate the flexible OFET sensor chip, we adopted high capacitance PVP:HDA as the dielectric layer to reduce the operation voltage, and the ITO-coated polyethylene terephthalate (PET) as the flexible substrate in OFET fabrication (Figure 5a). The transistor devices exhibited excellent transfer and output characteristics operating at low voltage (Figure 5b and **Figure S19**). Moreover, the ammonia sensing performance of low-voltage flexible devices (Figure 5c) was comparable to that of OFETs fabricated on SiO₂/Si substrates (Figure 3e). To demonstrate a clear path towards practical application in breath sensing, the effects of temperature and humidity fluctuations as well as mechanical bending on device response were further investigated. The porous DPP2T-TT devices exhibit excellent temperature stability within the range of breath temperature fluctuations (**Figure**

S20).^[50] The sensing performance is also stable against large fluctuations of environment temperature between 20~50 °C (**Figure S21**). In terms of humidity effect, human breath usually exhibits >80% relative humidity (RH)^[51], which does significantly impact the device performance (**Figure S22a**). However, such humidity effect can be fully compensated following an established procedure (**Figure S22b and S22c**).^[51] In other words, the current change to humidity and VOC is additive. Alternatively, the humidity effect can be eliminated via sample de-humidification (**Figure S23**).^[52] For further discussions on the humidity effect, see Supplementary **Note 4**.

We next investigated the selectivity of the flexible OFETs. Shown in **Figure 5d**, the nanoporous DPP2T-TT sensors exhibited high selectivity for ammonia among several major VOCs in breath tested at 1 ppm. On the other hand, we acknowledge that our selectivity test is not comprehensive as the human breath contains thousands of VOCs, mostly present at ppb levels. Moreover, multiple VOCs are expected to vary in concentrations with the onset of a disease, which further complicates the selectivity evaluation of a single component. Towards addressing this challenge, we performed preliminary studies on the impact of common confounding factors on selectivity towards ammonia, including multi-VOC background (**Table S11 and Figure S24**) and high sample humidity (**Figure S24**). We found that the selectivity for ammonia is not significantly altered by the presence of the VOC mixtures studied, nor by the high sample humidity within the range tested. We also studied the effect of substrate bending on charge carrier mobility and $\Delta I/I_0$ shown in Supplementary **Figure S25**.

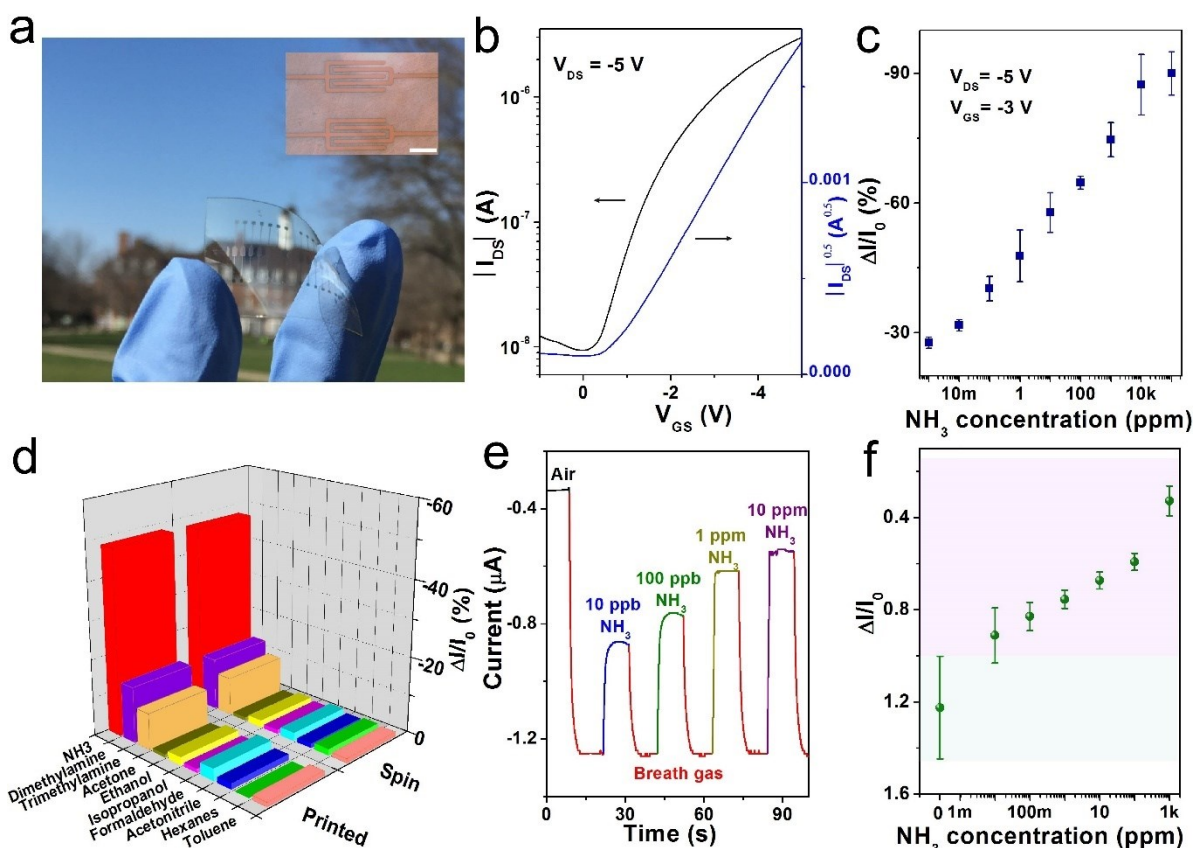


Figure 5. Flexible sensor chip. (a) Photograph of a flexible gas sensor. The devices were fabricated with a structure PET/ITO/PVP:HDA/porous PVP:HDA/DPP2T-TT/electrodes. DPP2T-TT were deposited via the printing method. (b) Transfer curve of the transparent OFET. (c) Current response of the porous DPP2T-TT devices for NH_3 . The average pore diameter is 600 nm. (d) Current responses of printed and spin-coated devices towards various VOCs at a concentration of 1 ppm. (e) Dynamic-sensing response curve of porous DPP2T-TT devices. Healthy breath sample (collected from a healthy female) was injected first. Subsequently, breath samples dosed with additional NH_3 at concentration of 10 ppb, 100 ppb, 1 ppm and 10 ppm was tested, to simulate the disease condition. (f) Comparison of current responses between healthy breath (without dosing NH_3 ; green background) and simulated breath gas with additional NH_3 dosed at various concentrations (pink background).

To test feasibility for breath sensing, we collected breath samples from a healthy female (age of 27) and simulated disease conditions by adding ammonia at a series of concentrations (10 ppb – 10 ppm). In the case of renal failure, the breath ammonia concentration of an individual increases by approximately 5-10 times relative to the healthy level; the extent of

increase ranges from hundreds of ppb to several ppm, which varies from subject to subject (Table S10). Accordingly, we designed our experiments to cover this entire range when simulating the ammonia concentration change in diseased patients. First, we established a baseline using health breath carrier gas. The exhaled breath sample contains a mixture of water vapor, carbon oxide, oxygen and thousands of VOCs.^[16, 49, 53] For the as-collected breath sample, the DPP2T-TT OFET sensors showed a positive response with an increase in current (Figure 5e). Repeated tests over a period of two weeks (sample collected at the same hour of the day) established a stable baseline and range of fluctuations of current responses to healthy breath for this individual (Figure 5f and **Figure S26**). We note that such stable response is attributed to the excellent stability of the fabricated DPP2T-TT transistor devices. For the simulated disease condition with elevated ammonia concentrations, we observed current responses clearly distinguishable from the baseline fluctuations, even when the ammonia concentration is increased by only 10 ppb (Figure 5e and **Figure S27**). Specifically, when the ammonia concentration increases by 1 ppm from the healthy level – a disease relevant condition, we observed a ~50% current change compared to the healthy condition (Figure 5f), which was well beyond the baseline fluctuations (Figure S26). In addition, across the wide range of concentrations tested, the magnitude of current response was fully consistent with the case when air was used as the carrier gas as opposed to the healthy breath sample (**Figures S28 and S29**).

We note that to realize breath sensing based health diagnosis, generally it is necessary to detect multiple VOCs in the presence of confounding factors using sensor arrays to yield a “breath fingerprint”. Combined with powerful statistical analysis algorithms (e.g. principle

component analysis, or PCA; discriminant factor analysis, or DFA), pattern recognition of the breath fingerprint can be carried out to differentiate healthy from diseased states. This approach has been developed and elegantly demonstrated employing nanomaterials based sensing platforms^[43-44, 54-55] and comprehensively summarized in recent review papers.^[15-16, 56] We expect that these methods for multi-VOC detection are transferrable to printed electronics. Sensor arrays have been extensively demonstrated using the printed electronics platform^[57]. Compared to nanomaterials based chemresistor sensors, OFET based sensors have their own advantages, such as chemical versatility, material synthesis directly through low-cost, high-throughput printing methods, diverse form factors and compatibility with the human body, as well as the capability to achieve self-powered multi-purpose sensing (chemical, pressure, temperature, strain etc) on the same platform.

3. Conclusions

In this work, we demonstrate, for the first time, tunable nanoporous organic semiconductor thin films fabricated using simple solution processing methods applicable to both polymer and small molecule semiconductors. Templated by the nanostructured PVP:HDA layer, the pore sizes in the semiconductor layer were widely tunable from 50 nm to 700 nm.

Introducing nanopores to DPP2T-TT based OFET sensors enhanced its reactivity towards ammonia by an order of magnitude, revealed by the reaction model we established. As a result, the nanopores enabled ultrasensitive, ultrafast response to ammonia below 1ppb at hundred-millisecond time scale, which is the best sensing performance reported so far.^{[12, 34-}

^{35]} We further validated the generality this strategy by fabricating nanoporous C₈-BTBT

OFET for formaldehyde sensing – a far more challenging sensing target as compared to ammonia due to its low reactivity. Again, we observed a 10-fold current-change enhancement with unprecedented sensitive response to analyte concentration below 1 ppb, which is three orders of magnitude improvement over the previously reported OFET formaldehyde sensors.^[17] We infer the following features to be critical for enhanced signal response of nanoporous OFETs: 1) the pores are through-pores to grant access to the highly reactive conducting channel at the semiconductor-dielectric interface; 2) the conjugated core of the semiconductor is oriented parallel to the pore wall to facilitate charge-transfer reaction with the analyte. Enabled by ultrasensitive chemical sensing, we demonstrated solution-processed flexible nanoporous sensor chip for real-time monitoring of breath ammonia concentration variations. The excellent performance, simple fabrication and diverse form-factors of nanoporous transistors may open up a wide range of applications in personalized health and environmental monitoring, frequently demanding sensitivity on the ppb level with fast response. Our approach of printing nanoporous thin films could be extended to other material systems and various solution processing methods. Furthermore, the concept of nanoporous organic electronics can bring novel properties beyond chemical sensitivity, such as enhanced mechanical stretchability, new optical properties, and even application in controlled drug release.

4. Experimental Section

Nanoporous device fabrication. Heavily doped silicon wafer (n-type) with a thermally grown SiO₂ (300 nm) were used as bottom-gate electrode and the dielectric layer, respectively. The

substrates were rinsed with toluene, acetone, and isopropyl alcohol, and dried with nitrogen before deposition of the organic materials. Poly-4-vinylphenol (PVP, $M_w = 25000$ mg/mL, Sigma-Aldrich) solution was spin-coated on the substrate at a rotation speed of 7000 rpm for fabricating the porous template. The solutions of PVP were prepared with 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (HDA, Sigma-Aldrich) in a series PVP:HDA ratio of 10:1 to 1:1 by weight in tetrahydrofuran (THF, Sigma-Aldrich). The concentrations of PVP range from 2.5 mg/mL to 20 mg/mL. Prior to spin-coating, the substrates were treated with plasma (Plasma Etch Inc. PE-25) for 6 min at 150 W. In order to obtain the porous structure, the humidity needs to be kept at 50% during the preparing process. Subsequently, the modified layer was cured at 100 °C in air for 1 h. For the nanoporous sensors fabrication, the templates were fabricated following the procedure above with PVP at a concentration of 5.5 mg/mL. After plasma treated for 12 s, the substrates were modified an octadecyltrichlorosilane (OTS, Sigma-Aldrich) assembly layer via vapor method.^[18]

OSC layers were deposited via meniscus-guided printing and spin-coating. The printing conditions were as the following: a silicon wafer with 300 nm SiO₂ treated with a monolayer of OTS was used as the printing blade; the gap distance between the substrate and the blade was set as 100 μ m; the blade was tilted by 7°; the substrate was kept at 25 °C. A 3 mg/mL DPP2T-TT/chloroform solution was used to deposit OSC films on the OTS modified template substrates, at printing speed of 0.5 mm/s. For C₈-BTBT, the thin film was deposited on the PVP:HDA template layer (without OTS) from 7.5 mg/mL chloroform solution at printing speed of 1 mm/s. In the spin-coating process, a DPP2T-TT/chlorobenzene solution (5

mg/mL) was dispensed on the substrate when the spin-coater motor was operating at a speed of 4000 rpm.^[18] The resulting DPP2T-TT film thickness was ~23 nm. C₈-BTBT/o-dichlorobenzene solution (5 mg/mL) was utilized to fabricate thin films by an off-center spin-coating method, wherein the substrate was offset from the center of the spin-coater.^[58]

Finally, gold source and drain electrodes (35 nm) were deposited on the DPP2T-TT thin film by vacuum evaporation through a shadow mask with a channel and width of 65 μ m and 4500 μ m respectively, while silver (35 nm) were thermally evaporated on C₈-BTBT surface as source and drain electrodes with the same pattern structure. The deposition rate was 0.5 Å/s. For formaldehyde sensor, polyethyleneimine (PEI)/water solution (Sigma-Aldrich, 0.2 mg/mL) was spin coated on the top of C₈-BTBT devices when the spin coater was rotated at a speed of 5000 rpm.

Fabrication of flexible devices. For flexible-sensor fabrication, the indium tin oxide (ITO) coated polyethylene terephthalate (PET) substrate (0.127 mm in thickness, Sigma-Aldrich) was cleaned with toluene, acetone and isopropyl alcohol. The substrate was treated with plasma for 6 min at 150 W, and the PVP:HDA solution (with a weight ratio of 10:1 in propylene glycol monomethyl ether acetate) was then utilized to fabricate the dielectric layer as previous reported.^[59] Following heat treatment at 100 °C for 1 h on the hot plate in air, the porous PVP:HDA template layer was spin-coated as described above. After the deposition of an OTS monolayer, DPP2T-TT (5 mg/mL, chloroform) solution was then printed onto the substrate at a speed of 0.5 mm/s. The patterned Au source-drain electrodes were finally thermally deposited onto the film with a thickness of 35 nm.

Film characterizations. The surface morphology and thickness of the modified layer and semiconducting layer were characterized with Asylum Research Cypher (Asylum Research) under the tapping mode. Synchrotron-based Grazing-incidence X-ray diffraction (GIXD) were performed at the small-wide-angle X-ray scattering beamline 8ID-E at the Argonne National Laboratory. For GIXD measurement, DPP2T-TT and C₈-BTBT were deposited on the pre-coated PVP:HDA template layer (with and without pores) via spin-coating and printing method. The substrate used for the samples was silicon wafers with 300 nm SiO₂. During the measurement, the samples were placed in a helium chamber. The sample to the Pilatus 1M detector distance was 208 mm, and the incidence angle was 0.2°. The X-ray beam energy was 7.35 keV, corresponding to a wavelength of 1.6868 Å. Integration of the diffraction peak areas was performed with the software GIXSGUI. To analyze the domain orientation, pole figures were constructed by extracting (010) π - π stacking peak intensities as a function of the pole angle χ , which are shown in Figure 2g and Figure S7g. The χ range was divided into 5° segments between 12.5° and 87.5°. To remove the strong background scattering from the underlying template layer, we performed careful peak deconvolution to extract the π - π stacking peak intensity. Multipeak fitting was performed on intensity vs. q curve of each segments to deconvolute the π - π stacking peak from the amorphous ring and the background scattering. The peak area was further normalized by film thickness and exposure time. The normalized intensity was further geometrically corrected to plot Figure 2g.

Electrical characterization of transistor devices. The OFET measurements were carried out in ambient air using an Keysight B1500A semiconductor parameter analyzer (Keysight Technologies) at room temperature. The mobilities were calculated from the equation $I_{DS} = (\mu W C_{eq} / 2L) (V_{GS} - V_T)^2$, where I_{DS} represent the source-drain current, μ is the mobility, W and L are the channel width and length, C_{eq} is the capacitance per unit area of the substrate, V_{GS} and V_T are the gate voltage and threshold voltage, respectively. In order to measure C_{eq} , a metal-dielectric layer-metal structure devices were constructed. The Keysight B1500A was used to carry out the Quasi-Static Capacitance Voltage (QSCV) measurement.

A polydimethylsiloxane (PDMS) micro-flow cell was laminated on the surface of the OFET to serve as a gas chamber above the channel region of the device with a size of $1.5 \times 1.5 \times 2 \text{ mm}^3$. A two-syringe push-pull syringe pump was connected to the flow cell with inlet and outlet polytetrafluoroethylene tubing. The sensing performance was monitored with the air-diluted analytes (by controlling volume ratio) at a constant flow rate of 5 mL/min. The dynamic sensing curves were collected using Keysight B1500A in real time. In the experiment, the humidity was controlled by humidifier and measured with a commercial humidity detector with an accuracy of 0.1%. We note that the sensor response time does not take into account the vapor delivery time.

Supporting information

Supplementary information is available from the Wiley Online Library or from the author.

Competing financial interests

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The authors declare no competing financial interests.

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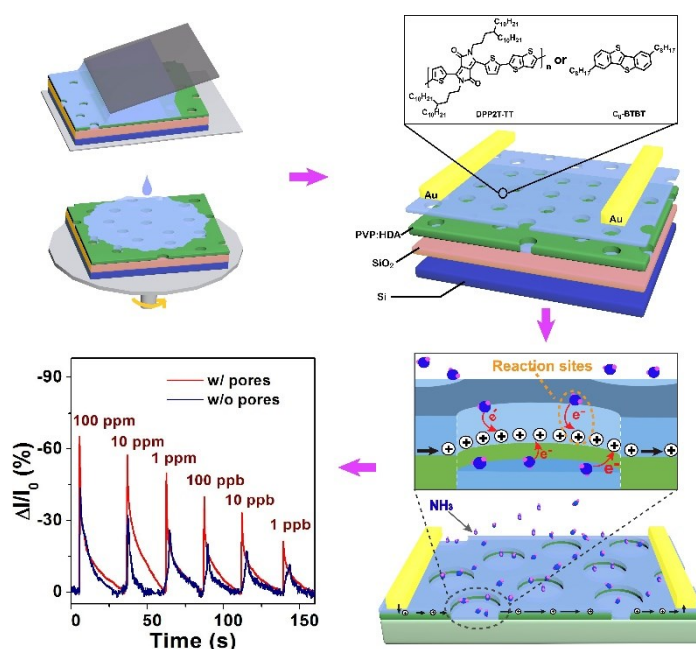
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Solution-Processed Nanoporous Organic Semiconductor Thin Films: Towards Health and Environmental Monitoring of Volatile Markers

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We demonstrate a generic method to solution process nanoporous thin films with pore sizes tunable from 50 to 700 nm for both polymer and small molecule semiconductors. The nanoporous transistor devices fabricated exhibit more sensitive and rapid detection of volatile

organic compounds below 1ppb at hundred-millisecond time scale. The nanopores function by exposing reactive sites in the conductive channel to the analytes.

Keyword

Solution process, Nanoporous film, Organic semiconductors, Gas sensor, Healthcare monitoring

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