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Supporting Information for:

Solution-Sheared Ultrathin Films for Highly-Sensitive Ammonia Detection using Organic Thin-Film Transistors

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1. Table S1 Sensing parameters of some NH_3 sensors using organic semiconductors, carbon, inorganic oxides as active materials.

Active Materials	Analyte/ Carrier Gas	Test Environment	Reported Detection Limit	Sensitivity ($\Delta I/I_0$ or $\Delta R/R_0$) (Corresponded Gas Concentration)	Response / Recovery Time	Selectivity	Stability	Reversibility	Fabrication of Active Layer	Ref
HTEB (Ultrathin Organic Film)	NH_3 / Air	Air, RT	0.1 ppm	89% (100 ppm) 82% (10 ppm) 64% (1 ppm) 57% (0.5 ppm) 41% (0.1 ppm)	(5–32) s / (55–100) s	Good	Good	Good	Solution-Shearing in air	This work
DTBDT-C6 (Ultrathin Organic Microstripe)	NH_3 / N_2	Air, RT	10 ppm	98.6–99.3% (50 ppm)	(5–45) s / (4–35) s	Good	Good	Good	Dip-Coating in air	13
NDI(2OD)(4tBuPh)-DTYM2 (Ultrathin Organic Film)	NH_3 / Air	Air, RT	10 ppm	50–70% (100 ppm)	~5 s / (10–20) s	—	—	Good	Spin-Coating and Annealing in air	14
CuPc-TPFB CoPc-TPFB (Ultrathin Organic Film)	NH_3 / N_2	Sealed chamber	0.45 ppm	CuPc-TPFB: 26% (0.45 ppm) 51% (4.5 ppm) CoPc-TPFB: 28% (0.45 ppm) 63% (4.5 ppm)	(90–120) s / > 300 s	Good	—	Good	Thermal Evaporation in vacuum	15
P3HT (Organic Film)	NH_3 / Air	Sealed Chamber	10 ppm	35% (100 ppm)	(30–200) s / (50~300) s	—	—	Good	Spin-Coating and Annealing	16
Pentacene (Porous Organic Film)	NH_3 / N_2	Sealed Chamber	0.5 ppm	23% (3 ppm)	~100 s / ~150 s	—	—	Good	Thermal Evaporation in vacuum	17
Graphene	NH_3 / Air	Air, RT for Chemisorption	0.5 ppm	17% (10 ppm)	> 3600 s / > 3600 s	—	—	Vacuum, ~200°C for Desorption	Chemical Vapor Deposition	18
SWCNT-PABS	NH_3 / N_2	N_2, 32°C	5 ppm	23% (100 ppm)	> 100 s / > 700 s	—	—	Good	Electric Arc Discharge	19
SiNW-Te NP	NH_3 / Air	shielded chamber	10 ppm	208% (400 ppm)	5 s / 8 s	—	—	Good	NP: Solution Method; SiNW: Thermal Evaporation	20

Some of the analyzed results are learned from Ref. 13.

—: Not available. RT: room temperature; NP: nanoparticle; NW: nanowire; IGZO: indium gallium zinc oxide; SWCNT: Single-walled carbon nanotube; PABS: poly-(m-aminobenzene sulfonic acid); SiNW: silicon nanowire

2. Molecular structures of organic semiconductors mentioned in Table S1.

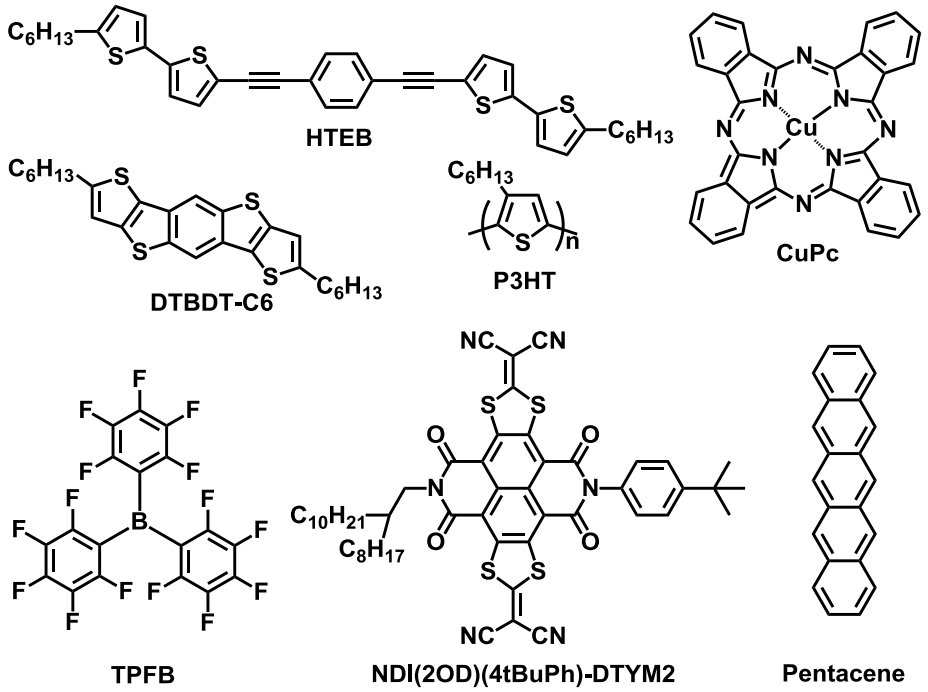

Fig. S1 Molecular structures of organic semiconductors mentioned in Table S1.

3. Representative output and transfer characteristics of bottom-gate top-contact (BGTC) organic thin-film transistors (OTFTs) with solution-sheared ultrathin films of HTEB.

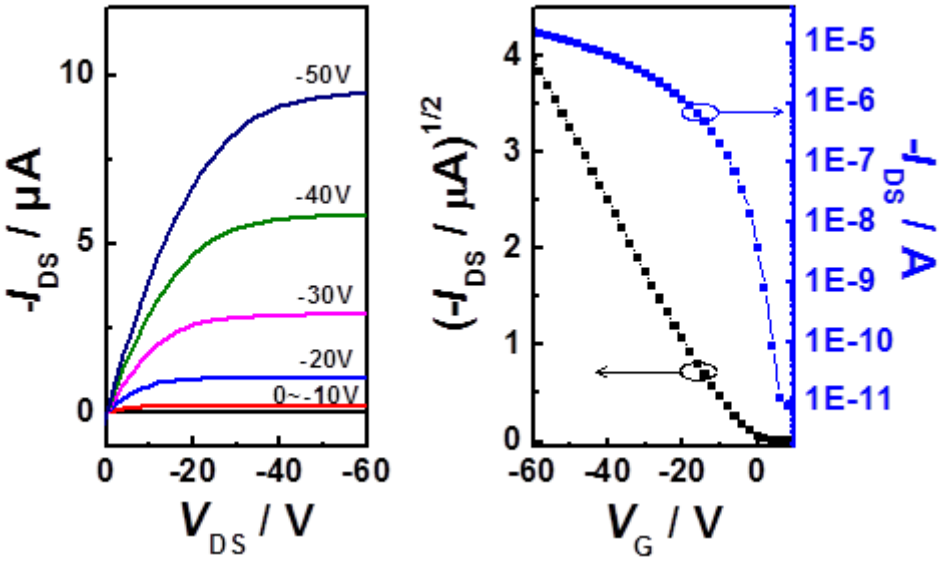

Fig. S2 Representative output and transfer characteristics of bottom-gate top-contact (BGTC) organic thin-film transistors (OTFTs) with solution-sheared ultrathin films of HTEB.

4. Transfer curves of BGTC OTFT upon exposure to different NH_3 concentrations.

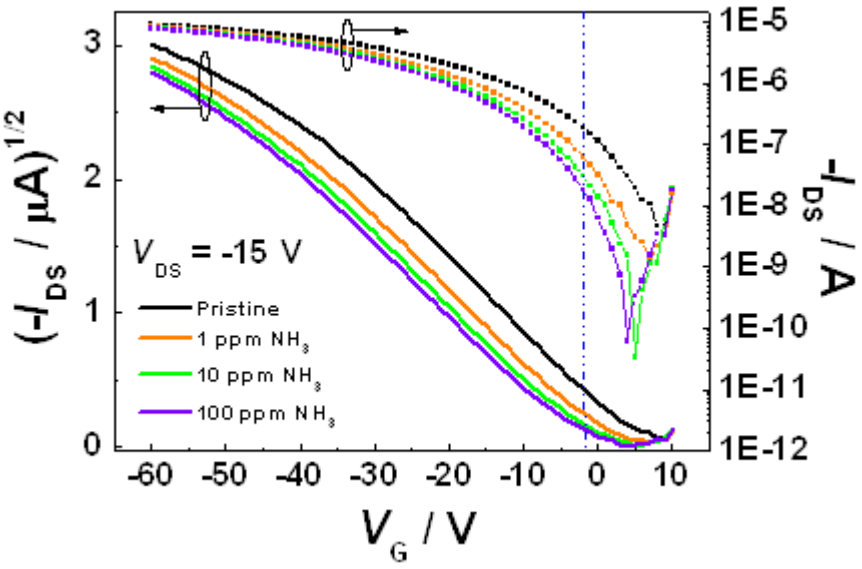

Fig. S3 Transfer characteristics of HTEB-based NH_3 sensor operated upon exposure to 0 ppm (black lines), 1 ppm (orange lines), 10 ppm (green lines) and 100 ppm (purple lines) NH_3.

As shown in Fig. S4, typical p-type field-effect characteristics could be observed at V_{DS} = –15 V. Upon exposure to NH_3, apparent electrical response (decrease of I_{DS} and shift of threshold voltage) could be observed, and the ΔI_{DS} became larger with the NH_3 concentration increasing. In the manuscript, all the sensing experiments were recorded at V_G = –2 V and V_{DS} = –15 V. The choosing criterion for bias voltage (V_G = –2 V) was to obtain a relatively high I_{DS} and a relatively large ΔI_{DS} simultaneously. The device sensitivity at V_G = –2 V and V_{DS} = –15 V was 65.8% (1 ppm), 83.7% (10 ppm) and 90.3% (100 ppm), respectively, corresponded very well with the results of Fig. 5b–c.

5. Optical microscope images and corresponded AFM images of BGTC OTFTs with 1–2, 3–4, 5–6 and 12–13 ML HTEB films.

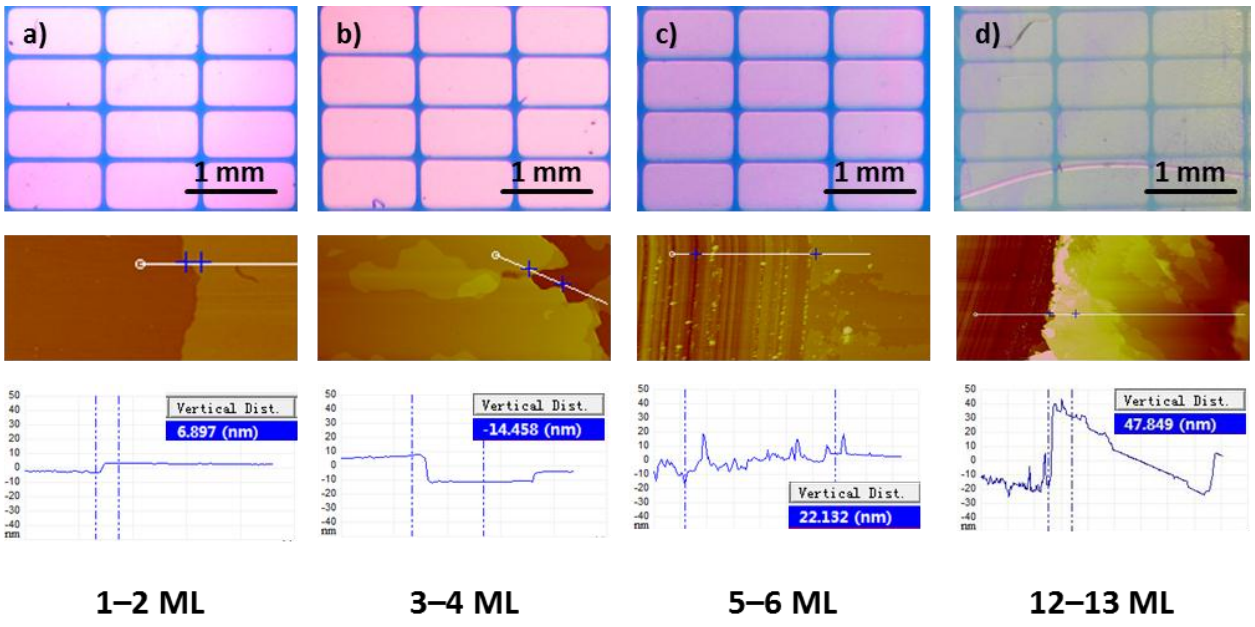

Fig. S4 Optical microscope images and corresponded AFM images of BGTC OTFTs with 1–2, 3–4, 5–6 and 12–13

ML HTEB films.

The deliberately scratched traces in (c) and (d) are made before deposition of Au electrodes to expose the substrates for investigation of film thickness.

6. Experimental

General fabrication of OTFTs: A silicon wafer with 300 nm-thick thermally grown oxide was used as substrate and dielectric. This wafer was rinsed in piranha solution (H_2SO_4: H_2O_2 = 7: 3) for 0.5 h, then successively cleaned with deionized water, acetone and ethanol, and dried under nitrogen. For BGTC OTFTs, the organic semiconducting layer was sheared onto the SiO_2/Si substrate, and then 20-nm source/drain electrodes (Au) were vacuum-deposited onto the semiconductor through a shadow mask. For BGBC OTFTs, 20-nm source/drain electrodes (Au) were pre-sputtered onto SiO_2/Si substrate, subjected for solution shearing of organic semiconductor.

The AFM characterization was carried out with a Digital Instruments Nanoscope III atomic force microscope in tapping mode. The XRD analyses were carried out in reflection mode at 40 kV and 200 mA with Cu Kα radiation as X-ray source. OTFT characteristics were recorded by a Keithley 4200 SCS at room temperature. Analyte gas (NH_3) was diluted from standard 1000 ppm NH_3 (in air) with air, and sensing performance of OTFT-based sensors was tested by Agilent B1500A in ambient conditions.