Supporting Information for:

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

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### Table S1 Sensing parameters of some NH$_3$ sensors using organic semiconductors, carbon, inorganic oxides as active materials.

<table>
<thead>
<tr>
<th>Active Materials</th>
<th>Analyte/Carrier Gas</th>
<th>Test Environment</th>
<th>Reported Detection Limit</th>
<th>Sensitivity (Δ$I/I_0$ or Δ$R/R_0$) (Corresponded Gas Concentration)</th>
<th>Response / Recovery Time</th>
<th>Selectivity</th>
<th>Stability</th>
<th>Reversibility</th>
<th>Fabrication of Active Layer</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTEB (Ultrathin Organic Film)</td>
<td>NH$_3$/Air</td>
<td>Air, RT</td>
<td>0.1 ppm</td>
<td>89% (100 ppm) 82% (10 ppm) 64% (1 ppm) 57% (0.5 ppm) 41% (0.1 ppm)</td>
<td>(5–32) s / (55–100) s</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Solution-Shearing in air</td>
<td>This work</td>
</tr>
<tr>
<td>DTBDT-C6 (Ultrathin Organic Microstripe)</td>
<td>NH$_3$/N$_2$</td>
<td>Air, RT</td>
<td>10 ppm</td>
<td>96.6–99.3% (50 ppm)</td>
<td>(5–45) s / (4–35) s</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Dip-Coating in air</td>
<td>13</td>
</tr>
<tr>
<td>NDI(2OD)(4tBuPh)-DTY M2 (Ultrathin Organic Film)</td>
<td>NH$_3$/Air</td>
<td>Air, RT</td>
<td>10 ppm</td>
<td>50–70% (100 ppm)</td>
<td>~5 s / (10–20) s</td>
<td>—</td>
<td>—</td>
<td>Good</td>
<td>Spin-Coating and Annealing in air</td>
<td>14</td>
</tr>
<tr>
<td>CuPc-TPFB CoPc-TPFB (Ultrathin Organic Film)</td>
<td>NH$_3$/N$_2$</td>
<td>Sealed Chamber</td>
<td>0.45 ppm</td>
<td>CuPc-TPFB: 26% (0.45 ppm) 51% (4.5 ppm) CoPc-TPFB: 28% (0.45 ppm) 63% (4.5 ppm)</td>
<td>(90–120) s / &gt; 300 s</td>
<td>Good</td>
<td>—</td>
<td>Good</td>
<td>Thermal Evaporation in vacuum</td>
<td>15</td>
</tr>
<tr>
<td>P3HT (Organic Film)</td>
<td>NH$_3$/Air</td>
<td>Sealed Chamber</td>
<td>10 ppm</td>
<td>35% (100 ppm)</td>
<td>(30–200) s / (50–300) s</td>
<td>—</td>
<td>—</td>
<td>Good</td>
<td>Spin-Coating and Annealing</td>
<td>16</td>
</tr>
<tr>
<td>Pentacene (Porous Organic Film)</td>
<td>NH$_3$/N$_2$</td>
<td>Sealed Chamber</td>
<td>0.5 ppm</td>
<td>23% (3 ppm)</td>
<td>~100 s / ~150 s</td>
<td>—</td>
<td>—</td>
<td>Good</td>
<td>Thermal Evaporation in vacuum</td>
<td>17</td>
</tr>
<tr>
<td>Graphene</td>
<td>NH$_3$/Air</td>
<td>Air, RT for Chemisorption</td>
<td>0.5 ppm</td>
<td>17% (10 ppm)</td>
<td>&gt; 3600 s / &gt; 3600 s</td>
<td>—</td>
<td>—</td>
<td>Vacuum, ~200°C for Desorption</td>
<td>Chemical Vapor Deposition</td>
<td>18</td>
</tr>
<tr>
<td>SWCNT-PABS</td>
<td>NH$_3$/N$_2$</td>
<td>N$_2$, 32°C</td>
<td>5 ppm</td>
<td>23% (100 ppm)</td>
<td>&gt; 100 s / &gt; 700 s</td>
<td>—</td>
<td>—</td>
<td>Good</td>
<td>Electric Arc Discharge</td>
<td>19</td>
</tr>
<tr>
<td>SiNW-Te NP</td>
<td>NH$_3$/Air</td>
<td>shielded chamber</td>
<td>10 ppm</td>
<td>208% (400 ppm)</td>
<td>5 s / 8 s</td>
<td>—</td>
<td>—</td>
<td>Good</td>
<td>NP: Solution Method; SiNW: Thermal Evaporation</td>
<td>20</td>
</tr>
</tbody>
</table>

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.

![Molecular Structures](image)

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.

![Transfer Characteristics](image)

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.

![Transfer curves](image)

**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 $V_{DS} = -15 \, \text{V}$. Upon exposure to NH$_3$, apparent electrical response (decrease of $I_{DS}$ and shift of threshold voltage) could be observed, and the $\Delta I_{DS}$ became larger with the NH$_3$ concentration increasing. In the manuscript, all the sensing experiments were recorded at $V_G = -2 \, \text{V}$ and $V_{DS} = -15 \, \text{V}$. The choosing criterion for bias voltage ($V_G = -2 \, \text{V}$) was to obtain a relatively high $I_{DS}$ and a relatively large $\Delta I_{DS}$ simultaneously. The device sensitivity at $V_G = -2 \, \text{V}$ and $V_{DS} = -15 \, \text{V}$ 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.

![Optical microscope images](image)

**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.
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$_2$SO$_4$: H$_2$O$_2$ = 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.