Electronic Supplementary Information

Phthalocyanine-mediated non-covalent coupling of carbon nanotubes with polyaniline for ultrafast NH\textsubscript{3} gas sensors

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Experiment details

1.1. Materials

1, 2, 4-Benzenetricarboxylic anhydride (97 % purity), urea (99 % purity) and ammonium chloride (99.5 % purity) were received from Aladdin Co. LLC. Ammonium molybdate tetrahydrate (99.9 % purity) was purchased from Sigma-Aldrich Co. LLC. All chemicals and solvents in this work were of analytical grade and were used as-received. The synthetic scheme of tetra-β-carboxyphthalocyanine cobalt(II) (TcPcCo) is shown in Scheme S1.

![Scheme S1](image_url)

Scheme S1. Synthetical scheme of tetra-β-carboxyphthalocyanine cobalt(II).

1.2. Instrument and methods

Elemental analyses of C, H and N were carried out on a Vario MICRO elemental analyzer. MALDI-TOF mass spectra was performed using a Bruker microflex LT (Bruker Daltonics) mass spectrometer. UV/Vis absorption spectra were recorded with a UV-2550 spectrometer (Shimadzu). FT-IR spectra were recorded on a Nicolet 6700 spectrometer (Thermo Fisher Scientific).

1.3. Synthesis of tetra-β-carboxyphthalocyanine cobalt(II) (TcPcCo)

1, 2, 4-Benzenetricarboxylic anhydride (1.92 g, 0.010 mol), anhydrous cobalt(II) chloride (0.39 g, 0.003 mol), urea (1.2 g, 0.020 mol), ammonium chloride (0.054 g, 0.001 mol) and ammonium molybdate tetrahydrate (0.06 g, 0.050 mmol) were taken into a solution of freshly distilled nitrobenzene (60 mL) at room temperature. Then, the mixture was stirred for 12 h in oil bath at 180 ºC. After natural cooling to about 20 ºC, the precipitate was filtered, washed successively with methanol, hydrochloric acid (1 mol L⁻¹), and water until the filtrate was colorless. The filter-cake was dried in a vacuum oven at 80 ºC for 6 h, and then dissolved in a solution of sodium hydroxide (2
mol L⁻¹, 60 mL) while stirring. Subsequently, the blue mixture was continuously stirred for 24 h in oil bath at 100 °C. After natural cooling to about 20 °C, the insolubles in the solution were removed by filtrating, and the filtrate was acidified by addition of concentrated hydrochloric acid to pH 3-4 with stirring, and left to stand overnight. Finally, the resulting precipitate was collected by centrifugation, washed with water until the pH of the supernatant approached 7 and then dried in a vacuum oven at 80 °C to obtained purple-black crystals of TcPcCo. Yield: 34.0 %. Anal. Calcd (found) C₃₇H₁₉N₈O₈Co: C, 58.30 (58.28); H, 2.49 (2.51); N, 14.74 (14.70). MALDI-TOF-MS Calcd (Found): m/z= 762.22(762.07) [M⁺]. Electronic absorption spectrum (UV-Vis) in DMF: λmax (nm) = 667, 606. FT-IR spectra (KBr pellets) ν: 3424, 1698, 1522, 1333, 1150, 1089, 945, 741 cm⁻¹.
Result and discussion

**Fig. S1** HRTEM images of MCNT (A) and MCNT@1.0PANI hybrid (B).

**Fig. S2** \( \text{N}_2 \) adsorption-desorption isotherms and pore-size distribution curves (the inset) of the MCNT and MCNT@1.0PANI hybrid.

**Fig. S3** SEM images of PANI NP (A) and MCNT/PANI hybrid (B).
**Fig. S4** SEM images of MCNT@0.5PANI (A) and MCNT@1.5PANI (B) hybrids.

**Fig. S5** UV-Vis spectra of TcPcCo, MCNT and TcPcCo/MCNT.

**Fig. S6** TGA profiles of TcPcCo, PANI NP, MCNT, TcPcCo/MCNT, MCNT@0.5PANI, MCNT@1.0PANI and MCNT@1.5PANI hybrids.
Table S1. The amount of PANI in MCNT@PANI hybrids.

<table>
<thead>
<tr>
<th>Sensing Material</th>
<th>Weight loss from 300 to 600 °C (wt%)</th>
<th>PANI content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI NP</td>
<td>26.65</td>
<td>100</td>
</tr>
<tr>
<td>TcPcCo/MCNT</td>
<td>3.12</td>
<td>0</td>
</tr>
<tr>
<td><a href="mailto:MCNT@0.5PANI">MCNT@0.5PANI</a></td>
<td>8.04</td>
<td>18.46</td>
</tr>
<tr>
<td><a href="mailto:MCNT@1.0PANI">MCNT@1.0PANI</a></td>
<td>11.50</td>
<td>31.44</td>
</tr>
<tr>
<td><a href="mailto:MCNT@1.5PANI">MCNT@1.5PANI</a></td>
<td>17.29</td>
<td>53.17</td>
</tr>
</tbody>
</table>

The weigh percent of TcPcCo assembled on MCNT has been evaluated by TG analysis under N\textsubscript{2} atmosphere. As shown in Fig. S6, TGA curve of TcPcCo presents a great loss of weight about 21.43 % from 300 to 600 °C sharply, indicating the thermal decomposition of peripheral carboxylic substituents in N\textsubscript{2} atmosphere. However, at the same temperature range, the weight loss of TcPcCo/MCNT is about 3.12 %; and only a minor weight loss averaging 2.00 % for MCNT, due to the destruction of the residual amorphous carbon. Taking into account the weight loss of MCNT, a corrected weight loss of 1.12 % can be estimated, which comes from TcPcCo in TcPcCo/MCNT. However, the actual amount of TcPcCo adsorbed on the surface of MCNT should consider the weight loss of TcPcCo itself. So, a real ratio of 5.23 % (1.12 %/21.43 %) can be calculated. Using the same calculation method, the weigh percent of PANI in MCNT@PANI hybrids are also evaluated by TG analysis under N\textsubscript{2} atmosphere (Fig. S6), and the results are shown in Table S1.

Fig. S7 XPS spectra of TcPcCo, PANI NP, MCNT and MCNT@1.0PANI hybrid.
Fig. S8 The real-time response curve of MCNT@0.5PANI (A), MCNT@1.5PANI (B), TcPcCo (C), PANI NP (D), MCNT (E), TcPcCo/MCNT (F) and MCNT/PANI (G) sensors upon exposure to 5-50 ppm NH₃.
Table S2. Comparison of the detection performances of TcPcCo, PANI NP, MCNT, TcPcCo/MCNT, MCNT/PANI, MCNT@0.5PANI, MCNT@1.0PANI and MCNT@1.5PANI sensors upon exposure to different concentrations of NH₃ from 5 to 50 ppm.

<table>
<thead>
<tr>
<th>Sensing Material</th>
<th>Response (%) /Detection conc. (ppm)</th>
<th>Response time (s)/Detection conc. (ppm)</th>
<th>Recovery time (s)/Detection conc. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TcPcCo</td>
<td>4.9/5; 10.32/10; 18.26/20; 23.08/50</td>
<td>49/5; 35/10; 30/20; 26/50</td>
<td>138/5; 165/10; 197/20; 239/50</td>
</tr>
<tr>
<td>PANI NP</td>
<td>4.1/5; 8.38/10; 13.18/20; 24.56/50</td>
<td>82/5; 72/10; 60/20; 51/50</td>
<td>625/5; 717/10; 814/20; 925/50</td>
</tr>
<tr>
<td>MCNT</td>
<td>2.84/5; 5.55/10; 8.08/20; 14.24/50</td>
<td>15/5; 12/10; 10/20; 9/50</td>
<td>157/5; 296/10; 429/20; 671/50</td>
</tr>
<tr>
<td>TcPcCo/MCNT</td>
<td>6.84/5; 14.76/10; 21.84/20; 29.4/50</td>
<td>47/5; 37/10; 31/20; 24/50</td>
<td>94/5; 185/10; 288/20; 502/50</td>
</tr>
<tr>
<td>MCNT/PANI</td>
<td>6.06/5; 11.01/10; 15.88/20; 26.84/50</td>
<td>72/5; 62/10; 47/20; 34/50</td>
<td>423/5; 454/10; 548/20; 718/50</td>
</tr>
<tr>
<td><a href="mailto:MCNT@0.5PANI">MCNT@0.5PANI</a></td>
<td>10.79/5; 24.02/10; 39.96/20; 63.5/50</td>
<td>28/5; 23/10; 20/20; 16/50</td>
<td>32/5; 43/10; 54/20; 61/50</td>
</tr>
<tr>
<td><a href="mailto:MCNT@1.5PANI">MCNT@1.5PANI</a></td>
<td>9.45/5; 19.53/10; 36.11/20; 56.29/50</td>
<td>38/5; 32/10; 29/20; 25/50</td>
<td>50/5; 62/10; 76/20; 83/50</td>
</tr>
<tr>
<td><a href="mailto:MCNT@1.0PANI">MCNT@1.0PANI</a></td>
<td>15.42/5; 32.89/10; 58.52/20; 92.15/50</td>
<td>9/5; 7/10; 6/20; 5/50</td>
<td>7/5; 9/10; 11/20; 12/50</td>
</tr>
</tbody>
</table>
Table S3. The relationship of the response of MCNT@1.0PANI sensor to varying concentration of NH$_3$.

<table>
<thead>
<tr>
<th>Sensing Material</th>
<th>The concentrations ranging of NH$_3$ is from 0.2 to 10 ppm</th>
<th>The concentrations ranging of NH$_3$ is from 20 to 200 ppm</th>
<th>detection limit (S/N = 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="mailto:MCNT@1.0PANI">MCNT@1.0PANI</a></td>
<td>$y = 3.187x + 0.656$ (R$^2 = 0.996$)</td>
<td>$y = 0.946x + 43.343$ (R$^2 = 0.998$)</td>
<td>36 ppb</td>
</tr>
</tbody>
</table>

Fig. S9 (A) The real-time response curve of MCNT@1.0PANI sensor to varying concentration of NH$_3$; (B) the response results of MCNT@1.0PANI sensor upon exposure to 250-400 ppm NH$_3$. 
Table S4. Room-temperature NH$_3$-sensing properties of different sensors.

<table>
<thead>
<tr>
<th>Sensing Material</th>
<th>Response (%)/Detection conc. (ppm)$^b$</th>
<th>Detection limit (ppm)$^b$</th>
<th>Response time (s)/Detection conc. (ppm)$^b$</th>
<th>Recovery time (s)/Detection conc. (ppm)$^b$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D sulfonated RGO hydrogel</td>
<td>7.1/20</td>
<td>1.48</td>
<td>16/20</td>
<td>~500/20</td>
<td>1</td>
</tr>
<tr>
<td>SnO$_2$-RGO</td>
<td>130/200</td>
<td>20</td>
<td>8/200</td>
<td>13/200</td>
<td>2</td>
</tr>
<tr>
<td>Fluorinated GO</td>
<td>121/500</td>
<td>0.006</td>
<td>86/500</td>
<td>116/500</td>
<td>3</td>
</tr>
<tr>
<td>PANI-TiO$_2$-Au</td>
<td>123/50</td>
<td>1</td>
<td>~52/50</td>
<td>~180/50</td>
<td>4</td>
</tr>
<tr>
<td>PANI films</td>
<td>~30/200</td>
<td>5</td>
<td>~210/200</td>
<td>~100/200</td>
<td>5</td>
</tr>
<tr>
<td>Au (III) complex</td>
<td>~28/80</td>
<td>2</td>
<td>8/80</td>
<td>11/80</td>
<td>6</td>
</tr>
<tr>
<td>Single ZnO-CNT</td>
<td>~640/100</td>
<td>0.2</td>
<td>20/100</td>
<td>420/100</td>
<td>7</td>
</tr>
<tr>
<td>ZnO/RGO</td>
<td>19.2/50</td>
<td>0.05</td>
<td>50/50</td>
<td>250/50</td>
<td>8</td>
</tr>
<tr>
<td>Ag-modified silicon nanowire</td>
<td>~340/10</td>
<td>0.33</td>
<td>~2/10</td>
<td>~9/10</td>
<td>9</td>
</tr>
<tr>
<td>Hierarchical GO–PANI hybrids</td>
<td>~60/100</td>
<td>0.1</td>
<td>36/100</td>
<td>18/100</td>
<td>10</td>
</tr>
<tr>
<td>RGO/bromophenol blue</td>
<td>~5.5/25</td>
<td>5</td>
<td>210/25</td>
<td>~3600/25</td>
<td>11</td>
</tr>
<tr>
<td>Ordered mesoporous carbons</td>
<td>~160/5</td>
<td>1</td>
<td>120/5</td>
<td>240/5</td>
<td>12</td>
</tr>
<tr>
<td>PANI/NiTSnPc</td>
<td>275/100</td>
<td>5</td>
<td>10/50</td>
<td>46/50</td>
<td>13</td>
</tr>
<tr>
<td>Au loaded ZnO nanostructures</td>
<td>~1546.5/100</td>
<td>5</td>
<td>~22/100</td>
<td>~57/100</td>
<td>14</td>
</tr>
<tr>
<td>Co$_3$O$_4$ nano-sheets</td>
<td>~860/100</td>
<td>0.2</td>
<td>~204/100</td>
<td>~835/100</td>
<td>15</td>
</tr>
<tr>
<td>RGO micro-pillars</td>
<td>88/40</td>
<td>~1</td>
<td>720/40</td>
<td>~3600/200</td>
<td>16</td>
</tr>
<tr>
<td>ZnO/NiO nanocrystals</td>
<td>42/50</td>
<td>15</td>
<td>26/50</td>
<td>150/50</td>
<td>17</td>
</tr>
<tr>
<td>PANI networks</td>
<td>~160/100</td>
<td>5</td>
<td>~80/100</td>
<td>~120/100</td>
<td>18</td>
</tr>
<tr>
<td>Material Description</td>
<td>LOD/LOQ</td>
<td>LOD/LOQ</td>
<td>LOD/LOQ</td>
<td>LOD/LOQ</td>
<td>a/b</td>
</tr>
<tr>
<td>----------------------------------------------------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>-----------</td>
</tr>
<tr>
<td>N-type CuTCNQ into p-type nitrogen-doped CuO</td>
<td>2.6/10</td>
<td>10</td>
<td>~200/10</td>
<td>~600/10</td>
<td>19</td>
</tr>
<tr>
<td>Cu$_2$O nanorods/RGO</td>
<td>104/200</td>
<td>100</td>
<td>28/200</td>
<td>~204/200</td>
<td>20</td>
</tr>
<tr>
<td>PANI fibers</td>
<td>~58/700</td>
<td>10</td>
<td>~28/700</td>
<td>~48/700</td>
<td>21</td>
</tr>
<tr>
<td>PANI@CeO$_2$ core-shell</td>
<td>650/50</td>
<td>2</td>
<td>57.6/50</td>
<td>~360/50</td>
<td>22</td>
</tr>
<tr>
<td>PANI/ZnO nanofibers</td>
<td>~240/100</td>
<td>25</td>
<td>~200/100</td>
<td>~600/100</td>
<td>23</td>
</tr>
<tr>
<td>PPy-Ag-SnO$_2$ nanofibers</td>
<td>131.85/100</td>
<td>0.02</td>
<td>~90/100</td>
<td>~180/100</td>
<td>24</td>
</tr>
<tr>
<td>Organic semiconductor film</td>
<td>30/10</td>
<td>10</td>
<td>~35/10</td>
<td>~48/10</td>
<td>25</td>
</tr>
<tr>
<td>RGO</td>
<td>23/2800</td>
<td>200</td>
<td>~600/2800</td>
<td>~1200/2800</td>
<td>26</td>
</tr>
<tr>
<td>MoS$_2$ sheets</td>
<td>~20/100</td>
<td>100</td>
<td>~200/100</td>
<td>Not fully recover</td>
<td>27</td>
</tr>
<tr>
<td>PANI-RGO hybrids</td>
<td>59.2/50</td>
<td>5</td>
<td>~204/50</td>
<td>Not fully recover</td>
<td>28</td>
</tr>
<tr>
<td>PPy nanostructures</td>
<td>95.1/100</td>
<td>0.02</td>
<td>~10/500</td>
<td>~180/500</td>
<td>29</td>
</tr>
<tr>
<td>PPy-s-CoPc hybrids</td>
<td>3.6/45</td>
<td>25</td>
<td>60/45</td>
<td>240/45</td>
<td>30</td>
</tr>
<tr>
<td>PPy films</td>
<td>16/40</td>
<td>3</td>
<td>~40/40</td>
<td>~540/40</td>
<td>31</td>
</tr>
<tr>
<td><a href="mailto:MCNT@1.0PANI">MCNT@1.0PANI</a></td>
<td>92.15/50;</td>
<td>0.036</td>
<td>5.0/50;</td>
<td>12/50;</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>140.99/100;</td>
<td></td>
<td>5.0/100;</td>
<td>12/100;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>228.87/200;</td>
<td></td>
<td>3.0/200;</td>
<td>13/200;</td>
<td></td>
</tr>
</tbody>
</table>

[a] If the sensor detection limit was not explicitly provided in the original report, then the lowest tested analyte concentration is listed.

[b] If the response (%), response time (s) or recovery time (s) of the sensor was not explicitly provided in the original report, then the estimate from the curve in that report is listed.
**Fig. S10** The response results of TcPcCo, PANI NP, MCNT and MCNT@1.0PANI sensors upon exposure to 200 ppm NO$_2$.

**Fig. S11** Response of the MCNT@1.0PANI sensor by varying RH from 0 % to 90 % (the concentration of NH$_3$ is 200 ppm) and the water contact angle of PANI-2.5TcPcCo hybrid (the inset image).

**Fig. S12** The electron transfer mechanism of MCNT@PANI sensors upon interaction with NH$_3$ and the interconversions of PANI between different structures.
Fig. S13 (A) SEM image of aMCNT@PANI hybrid; (B) UV-Vis spectra of PANI NP, aMCNT and aMCNT@PANI hybrid; (C) FT-IR spectra of PANI NP, MCNT, aMCNT and aMCNT@PANI hybrid; (D) TGA profiles of PANI NP, aMCNT and aMCNT@PANI hybrid.

The SEM images (Fig. S13A) show that the aMCNT@PANI hybrid also presents an evenly three-dimensional network-like nanostructures and the average diameter of it is about 20 nm. As shown in Fig. S13B, the characteristic broadening of PANI at 550 nm (benzoid–quinoid structure) can be observed in the UV-Vis spectrum of aMCNT@PANI hybrid, indicating the successful coating of PANI. Similar results can be observed by the typical FT-IR spectra (Fig. S13C). Obviously, the typical vibrations of PANI (1577 and 1498 cm\(^{-1}\) assigned to C=C and C–N stretching mode of vibration for the quinonoid and benzenoid) appear in the FT-IR spectrum of aMCNT@PANI hybrid. In addition, the typical bands of the carbonyl group (1708 cm\(^{-1}\) assigned to C=O stretching mode) can be observed on the aMCNT and aMCNT@PANI hybrid, demonstrating the successful preparation of aMCNT and the formation of covalent bonds between aMCNT and PANI. According to the TG curves, the calculated content of PANI in aMCNT@PANI hybrid is about 34.45 % (as shown in Fig. S13D and Table S5).
Table S5. The amount of PANI in aMCNT@PANI hybrid.

<table>
<thead>
<tr>
<th>Sensing Material</th>
<th>Weight loss from 300 to 600 °C (wt%)</th>
<th>PANI content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI NP</td>
<td>26.65</td>
<td>100</td>
</tr>
<tr>
<td>aMCNT</td>
<td>6.58</td>
<td>0</td>
</tr>
<tr>
<td>aMCNT@PANI</td>
<td>15.76</td>
<td>34.45</td>
</tr>
</tbody>
</table>

Fig. S14 The results of the response (A), response time (B) and recovery time (C) of MCNT@1.0PANI and aMCNT@PANI sensors upon exposure to 5-50 ppm NH₃.

Table S6. Comparison of the detection performances of aMCNT@PANI and MCNT@1.0PANI sensors upon exposure to different concentrations of NH₃ from 5 to 50 ppm.

<table>
<thead>
<tr>
<th>Sensing Material</th>
<th>Response (%) /Detection conc. (ppm)</th>
<th>Response time (s)/Detection conc. (ppm)</th>
<th>Recovery time (s)/Detection conc. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aMCNT@PANI</td>
<td>10.79/5; 23.02/10; 40.96/20; 64.50/50</td>
<td>57/5; 49/10; 37/20; 27/50</td>
<td>338/5; 363/10; 438/20; 574/50</td>
</tr>
<tr>
<td><a href="mailto:MCNT@1.0PANI">MCNT@1.0PANI</a></td>
<td>15.42/5; 32.89/10; 58.52/20; 92.15/50</td>
<td>9/5; 7/10; 6/20; 5/50</td>
<td>7/5; 9/10; 11/20; 12/50</td>
</tr>
</tbody>
</table>
**Fig. S15** The high-resolution O 1s XPS spectra (A) and I-V curves (B) of MCNT@PANI hybrids.

**Fig. S16** The high-resolution N 1s (A) and O 1s (B) XPS spectra of MCNT@1.0PANI sensor before and after exposure to NH₃ at room temperature.

**Table S7.** The high-resolution N 1s XPS results of MCNT@1.0PANI sensor before and after exposure to NH₃ at room temperature.

<table>
<thead>
<tr>
<th>Sensing Material</th>
<th>$-\text{N}^+=$ (at%)</th>
<th>Pyrrole N (at%)</th>
<th>$-\text{NH} -$ (at%)</th>
<th>$-\text{N}=$ (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong><a href="mailto:MCNT@1.0PANI">MCNT@1.0PANI</a></strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(before exposure to NH₃)</td>
<td>0.205</td>
<td>0.263</td>
<td>0.268</td>
<td>0.264</td>
</tr>
<tr>
<td><strong><a href="mailto:MCNT@1.0PANI">MCNT@1.0PANI</a></strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(after exposure to NH₃)</td>
<td>0.074</td>
<td>0.284</td>
<td>0.443</td>
<td>0.199</td>
</tr>
</tbody>
</table>
References


