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Copper (II) phthalocyanine supported on three-dimensional nitrogen-doped graphene/PEDOT-PSS nanocomposite as highly selective and sensitive sensor for ammonia detection at room temperature

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Abstract

Here we present a highly efficient ammonia (NH\textsubscript{3}) gas sensor made of copper (II) tetrasulfophthalocyanine supported on three-dimensional nitrogen-doped graphene-based frameworks (CuTSPc@3D-(N)GFs)/poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) nanocomposite sensing film with high uniformity over a large surface area. The NH\textsubscript{3} gas sensing performance of the nanocomposite was also compared with those of the sensors based on pure PEDOT-PSS and pristine CuTSPc@3D-(N)GFs. It was revealed that the synergetic behavior between both of the candidates allowed excellent sensitivity and selectivity to NH\textsubscript{3} gas in a low concentration range of 1–1000 ppm at room temperature. The CuTSPc@3D-(N)GFs/PEDOT-PSS
nanocomposite gas sensor exhibited much better (~5 and 53 times, respectively, with the concentration of NH$_3$ gas at 200 ppm) response to NH$_3$ gas than those of the pure PEDOT-PSS and pristine CuTSPc@3D-(N)GFs gas sensors. The combination of the CuTSPc@3D-(N)GFs and PEDOT-PSS facilitated the enhancement of the sensing properties of the final nanocomposite, and pave a new avenue for the application of CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite in the gas sensing field.

Keywords: CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite, Gas sensor, NH$_3$ detection, Conducting polymer
**Introduction**

Graphene, as a two-dimensional of sp$^2$ bonded carbon sheet, has attracted much attention in many diverse applications especially chemical sensors [1-8] owing to its excellent electronic, high mechanical stiffness and specific surface-to-volume ratio, as well as superior conductivity [9-12]. Three-dimensional (3D) graphene-based frameworks (3D-GFs) such as sponges, foams, and aerogels are an important class of new-generation porous carbon materials, which exhibit high porosity, large surface area, and high electrical conductivity [13-17]. These materials can serve as strong matrix for functionalizing metal, metal oxide, and electrochemically active polymers for various applications in electrochemical capacitors [18-20], batteries [21, 22], catalysis [23-25]. In the following, Dong et al. [26] demonstrated that 3D graphene electrode as an electrochemical sensor for detection of dopamine exhibited remarkable sensitivity (619.6 µA mM$^{-1}$ cm$^{-2}$) and lower detection limit (25 nM at a signal-to-noise ratio of 5.6), with linear response up to ~ 25 µM. Therefore, 3D-GFs can provide a promising platform for the development of high performance electrochemical sensors for dangerous volatile organic compounds (VOCs).

Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) as conjugated polymer (a mixture of two ionomers) has been extensively studied as the active material in sensing applications because of its good electrical conductivity, high transparency, low redox potential and good processability [27-29]. Nevertheless, its limited chemical and structural properties prevent its use in various practical applications especially electrochemical sensing [30]. It seems that the PEDOT-PSS composites with carbon nanostructures could be promising solution to its failures. In the following, Jian et al [31] used PEDOT-PSS composite film with O$_2$ plasma-treated single-walled carbon nanotubes for detection of ammonia (NH$_3$) and trimethylamine gases. Seekaew et al [27] reported the NH$_3$ sensing behavior of graphene-PEDOT-PSS composite film at room temperature. These evidence indicate that PEDOT-PSS composite films show potential as useful sensing materials, but their low sensitivity restrict their application in practical VOC sensors.

Because the above-mentioned reasons and also our interest in the synthesis of graphene based materials for various applications [25, 32-34], especially as new sensors [35-37], herein, we demonstrate the use of copper (II) tetrasulfophthalocyanine supported on three-dimensional
nitrogen-doped graphene-based frameworks (CuTSPc@3D-(N)GFs) and PEDOT-PSS nanocomposite as a novel gas sensor. This new architecture holds great appeal as a chemical sensor owing to large surface area, 3D multiplexed and highly conductive pathways, and continuously interconnected macroporous structures as well as modified active surface. To demonstrate its potential, we used it here for the detection of NH$_3$ as highly toxic gas which leads to irritates skin, eyes and respiratory tract of humans.

**Experimental**

**Preparation of CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite**

The CuTSPc@3D-(N)GFs were synthesized based on our previous work [25]. The obtained CuTSPc@3D-(N)GFs were dispersed in DI water (~ 1 mg/ml) and mildly sonicated for 30 min in a bath sonicator (EUROSONIC® 4D, 50 kHz). The PEDOT-PSS aqueous solution (weight ratio = 1-6, Clevios™ P VP AI 4083, solid content 1.3–1.7 %) was first dissolved in a DI water with a weight concentration of 89.82 %. The CuTSPc@3D-(N)GFs dispersion with 6 wt% Dimethyl sulfoxide (DMOS, Sigma-Aldrich Co) were added into the PEDOT-PSS solution and a homogeneous aqueous dispersion was obtained after 2 h stirring and sonicated for 30 min.

**Fabrication of CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor**

The nanocomposite gas sensor was prepared from PEDOT-PSS and CuTSPc@3D-(N)GFs materials with chemical structures schematically illustrated in Fig. 1. For fabrication of CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor, interdigitated Au electrodes with 100 nm thickness were deposited on a SiO$_2$/Si substrate (10×4 mm$^2$) by physical vapor deposition method. The prepared CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite solution was then drop casted over an interdigitated electrode (Fig. 2a). The width and inter-spacing of the electrodes are 200 µm and 400 µm, respectively. Then the nanocomposite gas sensor was backed for 1 h in furnace (Exciton, EX1200-4L) at 80 °C in nitrogen atmosphere (Fig. 2b). The pristine CuTSPc@3D-(N)GFs and PEDOT-PSS gas sensors were also fabricated and tested for comparison. The fabricated CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor is displayed in Fig. 2c,d.

**Characterization methods**

Transmission electron microscopy (TEM) was examined under LEO 912AB electron microscopy operated at an accelerating voltage of 120 kV. Scanning electron microscopy (SEM) was measured with S-4160 electron microscopy. Atomic force microscopic (AFM) images were
performed in the tapping mode with an ARA AFM (0201/A, Ara research Co, Iran). Brunauer–Emmett–Teller (BET) surface area measurements were carried out by nitrogen adsorption at 77 K using an ASAP2020 instrument. The conductivity of sensing films was measured by 4-point technique probe at 10 nA applied current. The sensor resistances were measured in a closed steel chamber (lab-made) with a LCR meter (Pintek-LCR900) and vapor gas flows were injected into the closed steel chamber by a mass flow meter (Alicat scientific, Tucson, USA). The reference humidity and sensor temperature were monitored by PT100 and HIH4000, respectively. The response and selectivity of the gas sensors were then assessed by the standard flow-through method towards NH$_3$, methanol, ethanol, acetone, toluene, chlorobenzene, and water with gas concentrations ranging from 1 ppm to 1000 ppm at room temperature. A constant flux of synthetic air of about 50 cm$^3$.min$^{-1}$ was mixed with the NH$_3$ gas source at different flow rate ratios to desired concentrations using mass flow controllers. All experiments were performed at room temperature (25 ± 2 °C) and the relative humidity of 10 ± 2 %. The sensitivity defined by the following equation:

$$\text{Sensitivity} = \frac{\Delta R}{R_0} \times 100$$  \hspace{1cm} (1)

and

$$\Delta R = R_{gas} - R_0$$  \hspace{1cm} (2)

where $R_0$ and $R_{gas}$ are the resistances of the sensor in synthetic air and test gas, respectively.

**Results and discussion**

The surface morphology of the CuTSPc@3D-(N)GFs has been presented in the SEM and TEM images of Fig. 3a-b, respectively. Fig. 3a exhibits the 3D morphology and an interconnected porous structure ultrathin graphene nanosheets. Moreover, the pore size ranges from a few hundred nanometers to several micrometers. Fig. 3b not only clearly shows the presence of mesopores in the carbon walls, but also reveals a wrinkled paper-like texture to the sheets, consistent with previous reports [38]. In addition, based on the BET method, the synthesized support (3D-(N)GFs) in our previous work has a high surface area (up to 266.0 m$^2$.g$^{-1}$) to put CuTSPc as active sensing sites. The chemical composition of 3D-(N)GFs and CuTSPc@3D-(N)GFs was confirmed by several characterization method such as elemental analysis, fourier
transform infrared spectroscopy, thermogravimetric analysis, X-ray powder diffraction and X-ray photoelectron spectroscopy [25].

Fig. 4a-b show the surface morphology of drop-coated pure PEDOT-PSS and CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite film, respectively. As can be seen that the pure PEDOT-PSS has relative smooth surface (Fig. 4a). On the other hand, Fig. 4b exhibits that the CuTSPc@3D-(N)GFs are uniformly dispersed into the PEDOT-PSS matrix without obvious agglomeration. This was ascribed to the hydrophilic nature of CuTSPc on the surface of the 3D-(N)GFs which not only ensured the strong bonding with PEDOT-PSS but also improved the dispersity and stability of the CuTSPc@3D-(N)GFs in aqueous solution (Fig. S1). Further roughness evaluations by AFM show that the average surface roughness ($R_a$) of pure PEDOT-PSS films is 1.98 nm while $R_a$ of the CuTSPc@3D-(N)GFs/PEDOT-PSS is 7.52 nm (Fig. S2). The much larger $R_a$ of CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite film compared to its PEDOT-PSS film suggests a significant enhancement of the active surface-area for gas adsorption by CuTSPc@3D-(N)GFs [25, 27].

Fig. 5a shows dynamic response of the CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor towards 1000 ppm NH$_3$ at room temperature in air. It exhibits that the sensor presents good repeatability of response towards repeated NH$_3$-sensing cycles at room temperature. The sensivity of the nanocomposite gas sensor increases upon exposure to NH$_3$ and recovers to the initial value upon the removal of NH$_3$ in air. As shown in Fig. 5b, the sensivity of the CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor increases dramatically when exposed to various concentrations of NH$_3$ ranging from 200 ppm to 800 ppm, and recovers towards the original values when NH$_3$ is replaced by air. The changing behavior of sensivity may be ascribed to the adsorption and desorption of NH$_3$ molecules of the nanocomposite sensing film [27]. The details of sensing mechanism for CuTSPc@3D-(N)GFs/PEDOT:PSS nanocomposite gas sensor will be discussed in further. In addition, the conductivities of pure PEDOT-PSS and CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite sensing films are 650 and 1430 Scm$^{-1}$, respectively. It indicates that the conductivity of pure PEDOT-PSS is increased by more than two factor, leading to significant increase of charge carrier concentration owning to CuTSPc@3D-(N)GFs incorporation. Therefore, CuTSPc@3D-(N)GFs shows a dominant effect in the charge transport through the PEDOT-PSS matrix.
The PEDOT-PSS based gas sensors usually operate at rather low temperatures with respect to gas sensors based on metal oxide [27, 35, 39]. It can be seen that the CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor shows low sensitivity to NH$_3$ with increase of temperature (Fig. 6). Therefore, the optimal temperature of the CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor for NH$_3$ detection was found to be room temperature. Since the interaction between CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite sensing film and volatile organic compounds (VOCs) gas is exothermic, the activation energy of desorption is larger than that of the adsorption NH$_3$ molecules of nanocomposite sensing film. This revealed that the decrease in sensitivity at higher temperatures is resulted from the higher desorption rate of NH$_3$ gas.

The response time of the pure PEDOT-PSS and CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensors are estimated to be ~ 6 min and ~ 2.5 min, respectively when it was experiencing the 95 % of the resistance change. Moreover, the recovery time of pure PEDOT-PSS and CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensors are ~ 2.5 min and ~ 1 min, respectively. Therefore, CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor indicates relatively short response and recovery times compared with PEDOT-PSS one (see Fig. 7).

Fig. 8 demonstrates the sensitivity of pure PEDOT-PSS, pristine CuTSPc@3D-(N)GFs and CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensors as function of NH$_3$ concentration at room temperature. At 1000 ppm NH$_3$ concentration, the sensitivity of pure PEDOT-PSS, pristine CuTSPc@3D-(N)GFs and CuTSPc@3D-(N)GFs/PEDOT-PSS gas sensors are 14.8 %, 9 %, and 91 %, respectively. At low concentration (50 ppm), the sensitivity as for mentioned gas sensors are 4 %, 0.35 %, and 9 %, respectively (inset of Fig. 8). As can be seen that the room temperature sensitivity of pure PEDOT-PSS is less high than that of CuTSPc@3D-(N)GFs, but its response is substantially increased after CuTSPc@3D-(N)GFs incorporation. Thus, CuTSPc@3D-(N)GFs improves NH$_3$ interaction leading the higher charge reduction only when it is included in PEDOT-PSS network. The detection limit of NH$_3$ for CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor is thus estimated to be 10 ppm at the room temperature.

Fig. 9 demonstrates the selectivity of the CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor to various VOCs vapors at concentration of 200 ppm. The sensitivity of the CuTSPc@3D-
(N)GFs/PEDOT-PSS nanocomposite gas sensor to NH₃, methanol, ethanol, acetone, toluene, chlorobenzene, and water are 18.7 %, 9.4 %, 5.5 %, 4.5 %, 2.3 %, 2.9 %, and 4.4 %, respectively. The CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor exhibits a remarkably high response to NH₃ and is almost sensitive to other VOCs vapors. The performance of the as-prepared nanocomposite gas sensor in this work was better than the previous reports in the literatures towards NH₃ detection (Table 1).

Table 1. Sensitivity (S), response time (R₁), recovery time (R₂), studied detection range (Dᵢ), materials (M) and measured temperature (Tₘ) of the various NH₃ gas sensors.

<table>
<thead>
<tr>
<th>Authors</th>
<th>S (%)</th>
<th>R₁ (s)</th>
<th>R₂ (s)</th>
<th>Dᵢ (ppm)</th>
<th>M</th>
<th>Tₘ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our work</td>
<td>8 (50 ppm), 91 (1000 ppm)</td>
<td>138</td>
<td>63</td>
<td>1-1000</td>
<td>CuTSPc@3D-(N)GFs/PEDOT-PSS</td>
<td>25</td>
</tr>
<tr>
<td>Xu et al. [40]</td>
<td>2 (10 ppm), 12 (70 ppm)</td>
<td>10</td>
<td>10</td>
<td>10-70</td>
<td>PEDOT nanowire</td>
<td>25</td>
</tr>
<tr>
<td>Kwon et al. [41]</td>
<td>2.1 (5 ppm), 24 (100 ppm)</td>
<td>&lt; 1</td>
<td>30</td>
<td>5-100</td>
<td>PEDOT nanotube</td>
<td>25</td>
</tr>
<tr>
<td>Seckaew et al. [27]</td>
<td>0.9 (5 ppm), 7 (1000 ppm)</td>
<td>180</td>
<td>----</td>
<td>5-1000</td>
<td>Graphene/PEDOT-PSS</td>
<td>25</td>
</tr>
<tr>
<td>Jian et al. [31]</td>
<td>0.1 (2 ppm), 33 (300 ppm)</td>
<td>12</td>
<td>18</td>
<td>2-300</td>
<td>SWCNTs/PEDOT-PSS</td>
<td>25</td>
</tr>
<tr>
<td>Yoo et al. [42]</td>
<td>0.015 (20 ppm), 0.075 (100 ppm)</td>
<td>100</td>
<td>700</td>
<td>0-100</td>
<td>pf-MWCNT/PANI</td>
<td>25</td>
</tr>
<tr>
<td>Tai et al. [43]</td>
<td>1.67 (23 ppm), 5.55 (117 ppm)</td>
<td>18</td>
<td>58</td>
<td>23-141</td>
<td>PANI/TiO₂</td>
<td>25</td>
</tr>
<tr>
<td>Matsughi et al. [44]</td>
<td>1.16 (500 ppm)</td>
<td>1500</td>
<td>-</td>
<td>-</td>
<td>PANI</td>
<td>30</td>
</tr>
<tr>
<td>Kebiche et al. [45]</td>
<td>7.1 (92 ppm)</td>
<td>834</td>
<td>600</td>
<td>92-4628</td>
<td>PANI</td>
<td>25</td>
</tr>
<tr>
<td>Hong et al. [46]</td>
<td>0.14 (20 ppm), 0.2 (100 ppm)</td>
<td>14</td>
<td>148</td>
<td>20-2000</td>
<td>Palladium/Polypyrrole</td>
<td>25</td>
</tr>
<tr>
<td>Crowley et al. [47]</td>
<td>0.24 (100 ppm)</td>
<td>90</td>
<td>90</td>
<td>1-100</td>
<td>Inkjet-printed PANI</td>
<td>80</td>
</tr>
<tr>
<td>Verma et al. [48]</td>
<td>0.9 (200 ppm)</td>
<td>1</td>
<td>420</td>
<td>50-200</td>
<td>PANI</td>
<td>25</td>
</tr>
<tr>
<td>Sengupta et al. [49]</td>
<td>2.3 (100 ppm)</td>
<td>120</td>
<td>300</td>
<td>100</td>
<td>PANI</td>
<td>25</td>
</tr>
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</table>

PANI: Polyaniline; SWCNTs: Single wall carbon nanotubes; MWCNT: Multi wall carbon nanotube

The improved NH₃ sensing properties of CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor are mainly ascribed to (i) the increased Rₐ in CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite sensing film compared with PEDOT-PSS one, (ii) inherently sensing properties of CuTSPc@3D-(N)GFs and (iii) π-π interaction by CuTSPc@3D-(N)GFs loading including 3D-(N)GFs as a support and Cu(II) complex as an active site in sensing film. (i) Since, the Rₐ of sensing film is directly proportional with gas sensitivity [27, 50], so the much larger Rₐ of CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite sensing film improves the active surface area
for gas adsorption (ii) It is well-known that graphene under ambient conditions behaves p-type semiconductors like conjugated polymers because their electronic properties can be reversibly controlled by doping/dedoping at room temperature [27, 51-53]. In addition, the electron-withdrawing sulfonic acid groups of the CuTSPc can be viewed as a charge delocalization of holes in the valence band. Therefore, when CuTSPc@3D-(N)GFs gas sensor is exposed to an electron donating gas like NH$_3$, proton transfer from the sulfonic acid groups of CuTSPc to the nitrogen atoms of NH$_3$ directly gives the self-doped zwitterionic form. Therefore, depletion of holes from the valence band of CuTSPc@3D-(N)GFs occurs, leading to a significant increase in resistance (iii) NH$_3$ molecules may interact with not only CuTSPc@3D-(N)GFs and PEDOT-PSS but also π-π bonding between CuTSPc@3D-(N)GFs and PEDOT-PSS [9]. Under the exposure to polar molecules like NH$_3$, the interaction not only can induce charge-transfer across delocalized π-electrons but also can lead to the formation of neutral polymer backbone and decrease in charge carries resulting in the improved sensing performances.

The NH$_3$ sensing mechanism of the CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor may be explained based on three possible mechanisms: (1) According to the reversible reaction [27, 45, 54]: CuTSPc@3D-(N)GFs/PEDOT-PSS− H$^+$ + NH$_3$ $\rightarrow$ CuTSPc@3D-(N)GFs/PEDOT-PSS + NH$_4^+$, the protons transfer from the sulfonic acid groups of CuTSPc to the nitrogen atoms of NH$_3$ molecules directly gives ammonium ions (NH$_4^+$). This process is reversible, and in fact, when NH$_3$ atmosphere is removed, the NH$_3$ molecules decrease the doping level of CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite sensing film by partially compensating for the influence of the initial dopants [55], which may change the resistance. (2) The NH$_3$ molecules are absorbed on the surfaces of CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite sensing film by physisorption, the holes of conductive CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite sensing film will interact with the electron-donating NH$_3$ analyte [27, 54]. The charge transfer from adsorbed NH$_3$ molecules not only increases the delocalization degree of conjugated π-electrons of nanocomposite sensing film, but also decreases the electrical conductivity of the nanocomposite sensing film [31, 41]. This mechanism is widely adopted for explanation of the change in conductivity of conductive polymer to acidic/basic analytes (doping/dedoping process). (3) The swelling of the CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite sensing film can increase the PEDOT distance and decrease the CuTSPc@3D-(N)GF’s conductive pathways, leading to significant increase in
resistance of the CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor upon NH$_3$ exposure and therefore enhanced NH$_3$ response.

**Conclusion**

In this work, novel NH$_3$ gas sensor based on CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite have been successfully fabricated and studied for the first time. The resultant CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite exhibited excellent sensitivity, dynamic behavior and selectivity to NH$_3$ owning possibly to the increase of the specific surface area, intrinsic sensing properties of CuTSPc@3D-(N)GF, and π-π interaction in CuTSPc@3D-(N)GFs/PEDOT-PSS. The nanocomposite gas sensor indicated much better (~ 5 and 53 times respectively with the concentration of NH$_3$ gas at 200 ppm) response to NH$_3$ gas than those of the sensors based on pure PEDOT-PSS and pristine CuTSPc@3D-(N)GFs. The response and recovery times of nanocomposite gas sensor (2.5 min, and 1 min, respectively) is much lower than that of pure PEDOT-PSS (6 min, and 2.5 min, respectively) towards 200 ppm NH$_3$. It demonstrates that the CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor which offers several distinct advantages on NH$_3$ detection over other fabricated sensors including high sensitivity, high productivity, low temperature processing and low cost, is expected to hold great promise for real-world applications.

**References**


Fig. 1 Schematic structures of (a) PEDOT-PSS, and (b) CuTSPc@3D-(N)GFs.
Fig. 2 Schematic steps of gas sensor fabrication process.
Fig. 3 Microstructure of as-prepared CuTSPc@3D-(N)GFs: (a) SEM, and (b) TEM images.
Fig. 4 SEM images of the pure PEDOT-PSS (a), and CuTSpC@3D-(N)GFs/PEDOT-PSS nanocomposite films (b).
Fig. 5 (a) Dynamic responses of the CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor to 1000 ppm NH$_3$, and (b) Sensivity of the CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor exposed to different concentrations of NH$_3$ at room temperature.
Fig. 6 Sensivity of the CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor as function of temperature towards 200 ppm NH$_3$. 

\[ \Delta R/R \]
Fig. 7 Response and recovery of gas sensors based on (a) pure PEDOT-PSS, and (b) CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite for 200 ppm NH$_3$ at room temperature.
Fig. 8 Sensitivity of pure PEDOT-PSS, pristine CuTSPc@3D-(N)GFs and CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensors towards 1-1000 ppm of NH₃ at room temperature.
Fig. 9 Selectivity of the CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor to various VOCs vapors of 200 ppm.
The novel CuTSPc@3D-(N)GFs/PEDOT-PSS nanocomposite gas sensor allowed excellent sensitivity and selectivity to NH$_3$ at room temperature.