O$_2$ plasma-functionalized SWCNTs and PEDOT/PSS composite film assembled by dielectrophoresis for ultrasensitive trimethylamine gas sensor

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A novel gas sensor based on composite films of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) and single-walled carbon nanotubes (SWCNTs) was fabricated for the detection of fishy trimethylamine (TMA) vapor. The SWCNTs were functionalized by O$_2$ plasma treatment to improve their solubility in the polymeric matrix, and alternative current dielectrophoresis was utilized for the first time to assemble the PEDOT/PSS–SWCNTs composite film to enhance the response to TMA molecules. The high resolution transmission electron microscopy (HR-TEM) images showed that the SWCNTs maintained their bulk structure after O$_2$ plasma functionalization. The scanning electron microscopy (SEM) images of the composite film showed that the oxidized SWCNTs were orderly arranged and uniformly dispersed into the polymer by dielectrophoresis. Compositional analyses of SWCNTs by X-ray photoelectron spectroscopy (XPS) suggested that O$_2$ plasma functionalization could remove amorphous carbon from the nanotube surface and introduce more hydrophilic oxygen-containing groups, leading to the improvement of SWCNTs solubility in the polymeric matrix. Gas sensitivities of the composite films largely relied on the treatment conditions. Compared to the raw or acid-treated SWCNTs-doped composite films, the film doped with SWCNTs modified by O$_2$ plasma at 30 W for 3 min exhibited the most sensitive and stable response characteristics to ppb-level TMA gas.

1 Introduction

The combination of conducting polymers (CPs) having extended delocalised π-orbitals along the polymer backbone and single-walled carbon nanotubes (SWCNTs) with unique symmetric all-carbon structures, endows the conjugated systems (CPs–SWCNTs) with large surface areas for gas absorption and the ability to effectively transport the charge carriers which are generated in the interactions between gas molecules and sensing films. Hence, gas sensors based on the CPs–SWCNTs composite films show sensitive responses to various gas species, in addition to other advantages such as good processability, high efficiency, and low power consumption. In recent years, poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) has been considered as a promising candidate for combination with nanotubes owing to its outstanding properties of high conductivity, chemical stability under ambient conditions, unique gas sensing response to polar gas molecules, and the surfactant-like nature for carbon nanotubes. However, the weak solubility and random dispersion of SWCNTs in the polymeric matrix are still the main obstacles to the CPs–SWCNTs composites.

The solubility of SWCNTs is largely reduced by the self-agglomeration of nanotubes and the weak bonding to polymers. Because of large specific surface areas, the inevitable self-agglomeration of SWCNTs leads to weak dispersion. The inactive outside layer of amorphous carbon on the intrinsic SWCNTs surface results in weak interfacial bonding between the nanotubes and the polymers. Typically, these situations can be overcome by oxidative functionalization of nanotubes through attaching various oxygen-containing groups on the nanotube surfaces. In addition, oxidizing treatments can alter the density of states of the nanotubes and improve the work function, leading to variation of the electronic properties of SWCNT bundles. Compared with the conventional oxidative modification by strong acids which will detrimentally damage the structures of SWCNTs, the gentle and non-polluting O$_2$ plasma treatment could maintain the bulk properties of the nanotubes without much structural destruction. It has been reported that O$_2$ plasma modification of CNTs strengthened the bonding between the nanotubes and polyaniline, and enhanced the response of the composite film to NH$_3$ gas.

On the other hand, improving the random dispersion of CNTs in the polymer matrix has recently received much attention, since the mechanical and electrical properties of polymer–CNTs composites are directly linked to the alignment of carbon
nanotubes in the matrix. As noted in previous reports on the orientation of CNTs in polymers, it is possible to align SWCNTs in poly(urethane) or poly(acrylate) by shear flow prior to polymerization. There have also been attempts to align MWCNTs in polymers by means of stretching or hot stretching. Solvent casting and melt-mixing of SWCNTs and PMMA in a hot-press have also been used to promote nanotubes alignment. Although some advances have been achieved, attempts to develop the simple, fast, low-cost and reproducible methods for alignment of CNTs in the polymers still remain a considerable technological challenge. In our work, alternative current dielectrophoresis (AC-DEP) was attempted to align the oxidized nanotubes in the polymer matrix for gas-sensing application. A previous study showed that AC-DEP assembly could align the SWCNTs dissolved in aqueous solution of sodium dodecyl sulfate and promote the electron-transfer efficiency between the electron-withdrawing gas molecules and the sensing film.

This study aims to develop a miniaturized chemiresistor sensor based on O₂ plasma-treated SWCNTs and PEDOT/PSS composite film assembled by AC-DEP for ultrasensitive sensing of trimethylamine (TMA) gas at room temperature. TMA is one of the volatile gases that causes pungent and fishy odors during the deterioration of dead fish or seafood, and its concentration is one of the essential indicators to assess the freshness of fish and seafood for the control of food quality and safety. It has been reported that the headspace TMA concentration from most fish species at the early stage of spoilage is at the ppb level.

2 Experimental section

2.1 Functionalization of SWCNTs

The raw SWCNTs were synthesized by catalytic chemical vapor deposition of acetylene (C₂H₂) over Fe–Mo–Co catalyst by using argon as carrier gas. The preparation of O₂ plasma-treated SWCNTs was achieved using the inductively coupled plasma. The radio frequency (RF) of the plasma was 13.5 MHz, the pressure was 10 Pa, and the O₂ flow rate was maintained at 10 sccm. The RF power was respectively fixed as 30 W and 50 W, and the treatment time was adjusted from 3 to 5 min. For the comparative trial, acid-treated SWCNTs were prepared by the mixture of H₂SO₄ and HNO₃ (1 : 3, v/v).

2.2 Fabrication of gas sensors based on PEDOT/PSS–SWCNTs composite

The preparation of the composite was based on our previous study. Firstly, a certain amount of the oxidized SWCNTs was mixed with the diluted PEDOT/PSS polymer (0.5 wt% for PEDOT and 0.8 wt% for PSS, Sigma) solution of 10 mL. After placing in an ultrasonic bath for 1 h, the blend was centrifuged at 10 000 rpm for 30 min. Then the supernatant (PEDOT/PSS–SWCNTs composite) of 10 µL was dropped onto an interdigitated microelectrode of Au metallic film that was patterned on the Al₂O₃ substrate by photolithography (Fig. 1). Both the width and the clearance of the electrode finger were 40 µm. To assemble the composite film, the electrode was placed in an AC electric field (voltage of 10 V and frequency of 5 MHz) for 3 min (Fig. 1a), and dried at 25 °C for 12 h. The possible arrangements of PEDOT/PSS and SWCNTs under the action of AC-DEP process were shown in Fig. 1b.

2.3 Analyses

High resolution transmission electron microscopy (HR-TEM) measurements of the SWCNTs samples were carried out by JEOL TECNAI G2 F20 (FEI, U.S.). Field emission scanning electron microscopic (FE-SEM) images of the samples were obtained by FEI Sirion FE-SEM (Netherlands). To evaluate the compositional changes on the SWCNT surface, X-ray photoelectron spectroscopy (XPS) analysis was performed with a system equipped with a hemispherical electron energy analyzer (VG ESCALAB MARK II) in a base pressure of 1 × 10⁻⁹ Torr. The photon source was a mono-chromatized Mg Kα line (hv = 1253.6 eV). In the spectrum analysis, the calibration of the energy scale was made relative to graphite (C 1s at 284.5 eV). The background signal was subtracted by Shirley’s method, the software Advantage 2.52 was used for peak fitting and quantitative analysis. The absorbance of the PEDOT/PSS–SWCNTs composite solution was recorded by an ultraviolet-visible light spectrophotometer (UV-2450, Shimadzu, Japan). Electrical characterization of PEDOT/PSS–SWCNTs composite film was measured using HP4284A LCR meters. The gas-sensing measurement was carried out in a sealed home-made gas flow-through chamber at room temperature (25 °C). The analyte gases of interest were obtained by controlling the flow rates of pure TMA gas and pure air (>99.99%) through mass flow controllers. Before the test, the chamber was fully purged by pure air (carrier gas) until a stable baseline was obtained. The response of the sensor was defined as (R – R₀)/R₀ × 100%, in which R₀ is the base resistance of the sensor in carrier gas and R is the stable resistance of the sensor exposed to the analyte gas.

3 Results and discussion

3.1 Microscopic analysis

Fig. 2 showed the typical HR-TEM images of raw SWCNTs (Fig. 2a) and plasma-treated SWCNT (Fig. 2b). Due to the serious self-agglomeration of the raw SWCNTs, it is very difficult to observe a single raw SWCNT. Fig. 2a showed tangled bundles of several raw SWCNTs, and the surface of the raw SWCNTs bundle was rough and vague. After the O₂ plasma functionalization, the dispersion of SWCNTs was improved, such that a
single oxidized SWCNT was easily observed, as shown in Fig. 2b. We can see that the plasma-treated SWCNT surface was comparatively smooth, which indicated the effective removal of amorphous carbons and impurities by oxygen plasma treatment. Additionally, the surface defects could be clearly found on the wall of the plasma-treated SWCNT. The oxygen-containing groups would be attached on these defects during the oxidation process. Moreover, Fig. 2b also showed that the gentle O₂ plasma treatment functionalized the nanotube without much structural destruction.

The area size of the PEDOT/PSS–SWCNTs composite film on the sensor’s substrate was 2 mm × 2 mm, and the average film thickness was approximately 200 nm. The morphologies of the PEDOT/PSS–SWCNTs composite films showed that the plasma-treated nanotubes were homogeneously distributed in the polymeric matrix without much agglomeration and overlap (Fig. 3). The oxidized SWCNTs were supposed to be integrated into the PEDOT/PSS polymeric matrix through strong π–π interactions with the thiophene rings of the PEDOT backbone as well as electrostatic interactions with the positively charged PEDOT, and thus became a part of the cross-linked structure in the hybrid composite system.⁹,₂⁹,₃₀

Compared to the random nanotubes in the drop-coated composite film (Fig. 3b, inset), the oxidized SWCNT were more likely to align regularly in the polymeric matrix under the electric field, and were mainly located between the large PEDOT/PSS grains (Fig. 3a). Due to the oxidized SWCNTs having a higher concentration of metallic nanotubes than the raw SWCNTs,¹¹ as well as the metallic SWCNTs having a larger real part of the Clausius–Mossotti factor than the semiconducting ones, the metallic oxidized SWCNTs were predicted to dominate the movement and were orderly arranged into bundles during the dielectrophoresis process (Fig. 3a, inset). In addition, certain PEDOT/PSS grains remaining on the surfaces of the nanotubes were forced to aggregate by the electric field force (Fig. 3a). Hence, SWCNTs should work as conjugated bridges and favor the nearest-neighbor electron tunneling of the grains and electron transmission at the interfaces.

Besides, the concentration of SWCNTs has a remarkable impact on the morphology of the composite film. When the SWCNTs loading in the AC-DEP assembled composite film increased from 1 mg mL⁻¹ to 10 mg mL⁻¹, the rough and nanostructured morphology of the film (Fig. 3a) became comparatively smooth and compact (Fig. 3c), which would impair the sensitivity of the gas-sensing film. Meanwhile, when the SWCNTs concentration was 10 mg mL⁻¹, the AC-DEP assembled composite film (Fig. 3c) showed more blocks than the drop-coated composite film (Fig. 3d). The phenomenon should be related to the AC-DEP assembly, which induced the rearrangement of the polymers into the blocks on the film surface. Also, it could be found that sufficient plasma-treated nanotubes can still uniformly disperse into the PEDOT/PSS matrix, implying strong binding between SWCNTs and PEDOT/ PSS (Fig. 3c and d).

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**Fig. 2** TEM images of the SWCNTs (a) before and (b) after O₂ plasma treatment.

**Fig. 3** SEM images of the AC-DEP assembled (a and c) and drop-coated (b and d) composite films doped with SWCNTs functionalized by oxygen plasma at 30 W for 3 min. The oxidized SWCNTs concentrations were respectively (a and b) 1 mg mL⁻¹ and (c and d) 10 mg mL⁻¹.
3.2 XPS analysis

The gross elements on the SWCNT surface were obtained through the survey spectra. The raw and plasma-treated SWCNTs samples showed the carbon (C 1s, C KLL) and oxygen (O 1s, O KLL) peaks, which indicated the primary constituents on the sample surface (see Fig. 4a and b). A slight oxygen peak at 534 eV was observed in the raw SWCNTs sample (Fig. 4a), which should be caused by the acid purification during the synthesis of the nanotubes. Peaks at 368.3 eV were caused by silver pastes which were used to fix the powder samples. After the plasma oxidation, the oxygen peak became strong and sharp, which showed the plasma treatment decorated the C–Ox groups on the SWCNT surfaces (Fig. 4b).

Detailed analysis of the C 1s spectra was performed to further explore the functional groups (see Fig. 4c and d). In the fitting procedure, the FWHM values were fixed at a maximum limit of 1.5 eV for all of the peaks. Fig. 4c showed that the result of peak fitting performed on C 1s spectrum yielded four peaks on the raw SWCNT surface. The peak at 284.0 ± 0.2 eV (1) matched with the sp²-hybridized graphite-like carbon (C=C). The peak at 285.0 ± 0.2 eV (2) corresponded to the sp³-hybridized diamond-like carbon (C–C). The peaks at 286.4 ± 0.2 eV (3) and 289.5 ± 0.2 eV (5) were attributed to hydroxyl groups (C–O) and carboxyl groups (O–C=O) respectively, which indicated the existing forms of the impurities.

Moreover, the large concentration of C–O in the raw SWCNTs suggested that the C–O groups have the higher interaction energy with the walls of the pristine nanotubes. After the O₂ plasma oxidation, the peak at 287.7 ± 0.2 (4) corresponding to carbonyl groups (C=O) (see Fig. 4d) was newly formed.

The peak assignments of the XPS C 1s spectra including the relative percentages of the components were summarized in Table 1. The content ratio of carbon to oxygen (C/O) was also calculated. The C/O obviously decreased after the oxidation, suggesting the efficient introduction of the oxygen-containing species.

For the plasma-oxidized SWCNTs, concentrations of the components varied with plasma powers and treatment time. At the same plasma power, percentages of C=C and C–C decreased with increasing treatment time while the content of the O=C=O group increased, but the ratio of oxygen to carbon decreased. When the plasma power increased at the same treatment time, the contents of C=C and C–C also decreased, and the ratio of C/O increased but then decreased at the treatment time of 5 min. In short, it could be confirmed that the plasma modification oxidized the C=C and C–C bonds, which would remove amorphous carbon layers from SWCNTs surfaces and decorate more oxygen-containing groups on SWCNT surfaces. For the acid-oxidized SWCNTs, the oxygen radicals were more likely to appear on the surfaces and tips of SWCNTs.

Fig. 4 The survey spectra and XPS C 1s core spectra of (a and c) raw SWCNTs and (b and d) plasma-treated SWCNTs.
leading to the maximum concentrations of the C=O and O–C=O groups as compared to the plasma-treated nanotubes (see Table 1). According to the smallest C/O, the acid treatment seemed to graft more functional groups on the SWCNTs surfaces, which implied that a large quantity of oxygen radicals was created in the oxidation process.

3.3 Absorbance of PEDOT/PSS–SWCNTs composites

The absorbance of the PEDOT/PSS–SWCNTs composite solution was studied to estimate the concentration of nanotubes in the polymeric matrix. The absorbance of the composite solutions increased after the plasma treatments (Table 1). It was verified by XPS spectra that the plasma treatment could remove the amorphous carbon and generate well-dispersed oxygen-containing defects on the SWCNTs surfaces. It was the oxygen-containing defects that provided the strong binding sites for PEDOT/PSS polymers and promoted the solubility of SWCNTs in the bulk matrix.\(^8\) In addition, the stronger plasma normally induced lower solubility of SWCNTs. This should be attributed to the agglomeration of SWCNTs with smaller diameters and shorter lengths, which was caused by the intensive plasma treatment.

3.4 Gas-sensing properties

3.4.1 Mechanisms of detection. The sensing mechanisms of functionalized-SWCNTs and PEDOT/PSS composite film assembled by AC-DEP could possibly be interpreted by the transduction principle in vertebrate olfactory receptor cells.\(^37\) The biomimetic material of PEDOT/PSS grains acted as the olfactory receptor neurons, and functionalized-SWCNTs, with good electrical properties, acted as the signal transduction pathway. When the electron-accepting PEDOT/PSS–SWCNTs composite film was exposed to the electron-donating TMA vapor, the electrons from methyl groups of TMA molecules combined with the holes of the p-type PEDOT/PSS grains, leading to the variations of delocalization degree of conjugated \(\pi\) electrons of PEDOT chains and the electrical response of the film. On the other hand, due to the metallic SWCNTs dominating the movement of SWCNTs bundles during the dielectrophoresis process,\(^25,31\) electrons from gas molecules should easily overcome the tunnel barriers and rapidly diffuse into the film predominately through the metallic SWCNTs pathway.\(^37\) Meanwhile, the alignment of metallic SWCNTs between Au electrodes could create a low resistance ohmic contact between the film and the electrodes substrate, and thus benefit the electron transfer through the composite system.

The response time, \(t_{50}\), of the AC-DEP assembled composite film was about 70 s, which was shorter than that (ca. 120 s) of the drop-coated film (Fig. 5). The result suggested that the AC-DEP assembly could boost the response rate of the composite film. Meanwhile, the response amplitude of the AC-DEP assembled film was increased by more than three times as compared with the drop-coated one. Additionally, the electrical properties of the AC-DEP assembled composite films were remarkably better than those of drop-coated films, which had been proved in our previous study.\(^8\)

3.4.2 Effects of plasma modification. Functionalization of SWCNTs by O\(_2\) plasma significantly affected the sensitivities of the DEP-assembled PEDOT/PSS–SWCNTs composite films for
TMA gas detection. Generally, the sensitivity of the composite film altered with different plasma powers and treatment times (Fig. 6a). The composite film doped with the SWCNTs treated by 30 W plasma showed higher sensitivity than those doped with the nanotubes treated by 50 W plasma. It was speculated that the stronger plasma induced the lower solubility of nanotubes in the polymeric matrix (Table 1) and reduced the diameters of nanotubes by peeling off much amorphous carbon from the nanotube surfaces, which damaged the electrical properties of the composite film. Additionally, the sensitivity of the composite film decreased with increasing treatment time. This should be related to the fact that the amount of oxygen-containing groups on the nanotube surfaces normally decreased as the treatment time increased, which would result in less active sites of the film for adsorption of gas molecules.

Furthermore, the composite film doped with SWCNTs treated by O₂ plasma at 30 W for 3 min exhibited the highest sensitivity to 6–90 ppb TMA gas, when compared with the films doped with other plasma-oxidized SWCNTs. This was possibly induced by the relatively high amounts of oxygen functional groups and the rational dispersion of SWCNTs, which optimized the active sensing sites and the conductivity of the composite film.

3.4.3 Comparison with other PEDOT/PSS–SWCNTs composite films. The gas-sensing properties of various composite films doped with raw or acid-treated SWCNTs, and without doping SWCNTs were also probed (Fig. 6b). Each data point along different curves in the figure was the average response of three sensors of the same type to the TMA at the same concentration. The film doped with 1 mg mL⁻¹ SWCNTs modified by O₂ plasma at 30 W for 3 min, showed the highest sensitivity to TMA vapors. The sensitivity of this film was more than 2 times greater than that of either the pristine PEDOT/PSS film or the film doped with acid-treated SWCNTs, and was over 3 times greater than that of the film doped with raw SWCNTs. The response of the AC-DEP assembled composite film to higher concentrations of TMA was shown in Fig. 6c. The full dynamic range of this sensor was 6–1000 ppb.

In the experiments, the color of the PEDOT/PSS solution in the region of electrode fingers deepened gradually with increasing time during the AC-DEP process. This reflected the aggregation and rearrangement of the PEDOT/PSS grains under the electric field, which would shorten the distance between the grains and boost the charge transport. Hence, the PEDOT/PSS film exhibited a sensitive response to TMA gas.

When doped with SWCNTs, the PEDOT/PSS polymers acted as a template for the embedding of nanotubes. The weak sensitivity of the composite doped with raw SWCNTs indicated the positive effects of oxidative functionalization. For the plasma-oxidized SWCNTs, the polymers were linked with the oxidized nanotubes via π-stacking and electrostatic interactions, and the 3D cross-linked nanostructure of the hybrid composite was formed. On the other hand, it was reported that the regular alignment of SWCNTs reduced the resistance of the film, which facilitated the electron diffusion at the interface where gas molecules reacted with the sensing film. Thus, the enhanced sensing areas as well as the fast and efficient electron diffusion ensured the high sensitivity of the composite film to TMA gas. For the acid-oxidized SWCNTs, the relatively weak sensitivity of the composite film was probably caused by the
overlap or entanglement of excessive nanotubes, increasing the difficulty in transporting the carriers.

The stabilities of various composite films for TMA gas sensing were also studied (Fig. 7). According to the variation of the response curve and the baseline drift, the PEDOT/PSS–SWCNTs composite film doped with the optimally plasma-oxidized SWCNTs showed the highest stability and the smallest baseline drift (Fig. 7a). The PEDOT/PSS film showed the largest baseline drift and the most irregular response to TMA gas (Fig. 7c). It should be noted that the film doped with raw nanotubes presented a slight and extremely unstable gas sensing response. The sources of baseline drift in gas sensors mainly include electrical, thermal, and analyte-induced instabilities.\(^\text{38}\) In our work, a fixed potential of 6 V was employed to measure the sensor resistance. The potential may be too large to generate high heating power on the composite film with small resistance and lead to an increase in the temperature of the p-type film. So the base resistance of this film-based gas sensor decreased and thus a down-drift tendency of the baseline was induced after long operation times. Our experimental results showed that the baseline drift was minimized when the fixed potential was reduced to 0.2 V. But the baseline drift of the as-prepared sensor is still inevitable after long operation times. Thus, for the practical application, the electric circuit should be designed to track the baseline drift and reset when needed, or appropriate sensor signal processing methods should be chosen to correct the baseline drift.

In addition, the selectivity of the sensor should be taken into account. Since the concentrations of other methyl-group-containing gases, such as dimethylamine and methylamine, emitted during the deterioration of dead fish or seafood are low enough to be neglected,\(^\text{26}\) attention should be paid to the effect of atmospheric humidity on the response of the sensor for feasibility of application.

The response of the optimal film-based sensor to varied relative humidity (RH) in the air stream was shown in Fig. 8a. The optimal film was prepared by assembling the PEDOT/PSS–SWCNTs composite in which the SWCNTs were treated by O\(_2\) plasma at 30 W for 3 min. The response slope of the sensor for RH (slope\(_{\text{RH}}\) = 5.9467) was about 100-fold larger than that for ppb-level TMA vapors (slope\(_{\text{TMA}}\) = 0.058). Such a great sensitivity of the sensor to the moisture should be ascribed to the hydrophilic PSS polyelectrolyte. The decrease of the conductivity upon exposure to water molecules was attributed to the depletion of hole concentration in the composite film as a result of the adsorption of H\(_2\)O molecules.

The response behaviors of the as-prepared sensor to TMA vapors in a humid environment at room temperature were explored (Fig. 8b). The sensor response increased with increasing RH. As the TMA concentrations with the same relative humidity increased, the sensor response came down, while the sensor response to dry TMA vapor went up (Fig. 6b). Such a phenomenon should be related to the strong competitive sorption of TMA and H\(_2\)O molecules onto the sensing film. In the absence of TMA molecules, the H\(_2\)O molecules absorbed into the sensing film would deplete the hole concentration, and thus cause a great sensor response. When TMA vapor was presented, the TMA molecules competed with H\(_2\)O molecules and partially substituted for H\(_2\)O molecules to land on and react with the composite film. As the sensitivity of the sensor to TMA vapor was far lower than to the moisture, the sensor response was reduced with the increasing TMA concentrations under different humidity levels. The fitting results of the sensor response to TMA vapors with the humidity effects were presented in Fig. 8c.
Moreover, the life-span study of the films showed that the PEDOT/PSS films chapped and shed from the substrate after one-month storage at room temperature, while the PEDOT/PSS–SWCNTs composite films maintained good surface morphology on the substrate over six months. The result should be ascribed to the high elastic modulus of SWCNTs which enabled much stronger and more stable composite films.

Compared with the previously reported sensors\textsuperscript{26,39,40} for TMA detection, the as-prepared sensor in our work exhibited a more sensitive and stable response to TMA gas at ultra-low concentrations. It should be pointed out that the analyte gases need to be dehumidified before the detection, or a proper humidity sensor should be used to compensate for the humidity effects. In the next sensor design, due to the highly conductive property and the ability to act as an effective dispersant of SWCNTs,\textsuperscript{41,42} hydrophobic room-temperature ionic liquids can be incorporated into the composite film to minimize the humidity effects while maintaining the sensitivity of the sensor.

**Fig. 8** The responses of the optimal film-based sensor to (a) varied relative humidity (RH), (b) TMA vapors in humid environments at room temperature, and (c) the fitting results of the sensor response to TMA vapors with the humidity effects.
4 Conclusions

In this study, SWCNTs were functionalized by O2 plasma treatment, and PEDOT/PSS–SWCNTs composite films were prepared as the gas-sensing layer via AC-DEP assembly. To the best of our knowledge, this is the first report to assemble the CPs and functionalized SWCNTs composite film using dielectrophoresis. Concomitant to the homogenous distribution and orderly arrangement of SWCNTs, partial PEDOT/PSS grains were inclined to aggregate into larger ones under the electric field, turning the nanotubes into the conjugated bridges which facilitated the nearest-neighbor electron tunneling of the grains. The hydrophilic carbonyl groups were newly grafted on the SWCNT surfaces after plasma functionalization. It was the increased ratio of oxygen to carbon that enhanced the solubility of SWCNTs in the polymeric matrix. The film doped with the SWCNTs functionalized by O2 plasma at 30 W for 3 min exhibited the most satisfactory response to ppb-level TMA gas at room temperature. These findings will help in optimizing the CPs–SWCNTs composite films for ultra-sensitive detection of TMA gas at room temperature, based on functionalization of SWCNTs by O2 plasma and assembly of CPs–SWCNTs composites using dielectrophoresis.

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