Low-cost and flexible printed graphene–PEDOT:PSS gas sensor for ammonia detection

Yotsarayuth Seekaew \textsuperscript{a}, Shongpun Lokavee \textsuperscript{b}, Ditsayut Phokharatkul \textsuperscript{c}, Anurat Wisitsoraat \textsuperscript{c}, Teerakiat Kerdcharoen \textsuperscript{b,d}, Chatchawal Wongchoosuk \textsuperscript{a,*}

\textsuperscript{a} Department of Physics, Faculty of Science, Kasetsart University, Chatuchak, Bangkok 10900, Thailand
\textsuperscript{b} Materials Science and Engineering Programme, Faculty of Science, Mahidol University, Bangkok 10400, Thailand
\textsuperscript{c} Nanoelectronics and MEMS Laboratory, National Electronics and Computer Technology Center, Klong Luang, Pathumthani 12120, Thailand
\textsuperscript{d} Department of Physics and Center of Nanoscience and Nanotechnology, Faculty of Science, Mahidol University, Bangkok 10400, Thailand

\textbf{A R T I C L E I N F O}

Article history:
Received 14 May 2014
Received in revised form 25 August 2014
Accepted 26 August 2014
Available online 10 September 2014

Keywords:
Printed electronics
Flexible sensor
Conducting polymer
PEDOT:PSS
NH\textsubscript{3} sensor

\textbf{A B S T R A C T}

This work presents a simple, low-cost and practical inkjet-printing technique for fabricating an innovative flexible gas sensor made of graphene–poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) composite film with high uniformity over a large area. An electronic ink prepared by graphene dispersion in PEDOT:PSS conducting polymer solution is inkjet-printed on a transparency substrate with prefabricated electrodes and investigated for ammonia (NH\textsubscript{3}) detection at room temperature. Transmission electron microscopy, Fourier transform infrared spectroscopy, UV–visible spectrometer and Raman characterizations confirm the presence of few-layer graphene in PEDOT:PSS polymer matrix and the present of $\pi$–$\pi$ interactions between graphene and PEDOT:PSS. The ink-jet printed graphene–PEDOT:PSS gas sensor exhibits high response and high selectivity to NH\textsubscript{3} in a low concentration range of 25–1000 ppm at room temperature. The attained gas-sensing performance may be attributed to the increased specific surface area by graphene and enhanced interactions between the sensing film and NH\textsubscript{3} molecules via $\pi$ electrons network. The NH\textsubscript{3}-sensing mechanisms of the flexible printed gas sensor based on chemisorbed oxygen interactions, direct charge transfers and swelling process are highlighted.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Printed electronics is an emerging technology that allows the replacement of traditional inflexible silicon-based electronic devices with low-cost flexible organic-based counter parts. In addition, it can be extended to a number of new application areas such as biodegradable electronics and wearable electronics. From IDTechEx report, the market of printed, flexible and organic electronics is rapidly growing and may reach up to $76.79 billion in 2023 \cite{1}. Thus, development of printed electronic technology has recently earned great attention. Printable electronic ink is one of the most important components of printed electronic technology. Recent research on printed electronic inks has been mainly focused on developing novel ink materials that provide advanced functionality and high performances but are easy to process, lightweight and low cost. An effective and practical approach to advanced printable ink is the combination of functional polymers or organic material and other functional inorganic nanomaterials by solution processing.

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is a conjugated polymer (a mixture of two ionomers) widely used as the active material in flexible and printed electronics because of its good electrical...
conductivity, high transparency, low redox potential and good processability [2,3]. However, its limited structural and chemical properties remain major obstacles that inhibit its use in various practical applications [4]. Its combination with novel carbon nanostructures may be a potential solution to the shortcomings. Graphene, a novel carbon nanostructure with a densely packed honeycomb two-dimensional lattice, has recently emerged as a highly promising material for many applications including nanoelectronics, flexible electronics, batteries, supercapacitors, solar cells, gas and chemical sensors [5–9] due to its unique properties such as large specific surface area, high electrical conductivity, excellent electron transfer rate and high mechanical strength [10]. Therefore, graphene has recently been incorporated into PEDOT:PSS by different methods and characterized for various electronic applications. For example, high quality graphene–PEDOT nanocomposite film was synthesized based on simultaneous electrodeposition of PEDOT and electrochemical reduction of graphene oxide on a glassy carbon electrode for biosensing applications [8]. In addition, a double-layered graphene/PEDOT:PSS conductive film was fabricated and its optical and electrical properties were characterized for large-area flexible optoelectronic devices [4]. Moreover, graphene–PEDOT:PSS was reported to provide improved performances for the counter electrodes of dye-sensitized solar cells and working electrodes of electrochemical sensors [7,11–13]. However, to the best of our knowledge, there has been no report of flexible gas sensor based on graphene–PEDOT:PSS material.

Gas-sensing film can generally be prepared by several techniques including reactive sputtering [14], thermal evaporation [15], spin coating [16], chemical vapor deposition [17] and screen printing [18]. However, some of them do not support the preparation of sensing film on flexible substrates such as paper or plastic. In addition, they suffer from several disadvantages such as high cost, high complexity, long operating time, poor reliability and low productivity. Recently, ink-jet printing technique has been proposed as a promising method for gas sensor preparation because of its unique advantages including simplicity, low-temperature processing, high productivity, low-cost and low material waste [19]. The method operates by ejecting ink through very fine nozzles with 10–200 μm in diameters into a series of droplets deposited on substrates [20,21]. It can control deposition of functional materials with arbitrary geometry on various types of substrate.

In this work, we report the first application of ink-jet printing for fabrication of a low-cost and flexible graphene–PEDOT:PSS gas sensor. A solution-processed graphene–PEDOT:PSS ink is inkjet-printed on a transparency substrate with prefabricated electrodes and investigated for NH3 detection at room temperature.

2. Experimental details

2.1. Preparation of electronic ink

The electronic ink was prepared from PEDOT:PSS and graphene materials with chemical structures schematically illustrated in Fig. 1. The PEDOT:PSS aqueous solution (Cleviosa™ P VP AI 4083, solid content 1.3–1.7%, PEDOT:PSS weight ratio = 1:6) was purchased from Heraeus Precious Metals GmbH & Co., KG. The graphene powder (graphene nanoplatelets grade 3, specific surface areas of 600–750 m2/g, an average thickness of 8 nm, conductivity of 7.813 × 104 Sm–1 and typical particle diameter of less than 2 μm) was acquired from Cheap Tubes Inc. Other reagents and solvents were purchased from Sigma–Aldrich and used without any further purification. For preparation of the graphene–PEDOT:PSS ink, PEDOT:PSS was first dissolved in a mixture of solvents with a weight concentration of 89.82%. The solvent mixture contains 5.98 wt.% of dimethyl sulfoxide (DMSO), 3.99 wt.% of ethylene glycol (EG) and 0.199 wt.% of triton x-100. It should be noted that DMSO was used as the primary solvent that exhibits good conductivity and low baseline resistance at room temperature [22], while EG and triton x-100 were added to improve of the viscosity and surface tension as well as to prevent of rapid drying and clogging in the printer head [23]. The final PEDOT:PSS solution was thoroughly stirred for 30 min at room temperature. To prepare graphene solution, 10 mg of chemically synthesized graphene powder was dispersed in 5 ml of DMSO. The graphene solution was then thoroughly sonicated for 30 min and stirred for 24 h at room temperature. Next, graphene solution was mixed with 40 ml of PEDOT:PSS. To avoid agglomeration of graphene, PEDOT:PSS in designed chamber was placed in an ultrasonication bath (40 kHz) and graphene solution was gradually dripped into PEDOT:PSS with the rate of 25 μl/s. The final graphene–PEDOT:PSS solution (2.33 wt.% of graphene to the total solid content of PEDOT:PSS) was thoroughly sonicated for 30 min and stirred for 1 h at room temperature.

2.2. Fabrication of graphene–PEDOT:PSS gas sensor

For fabrication of flexible gas sensors, interdigitated electrodes with 1 mm interdigit spacing were deposited on a flexible and transparent substrate by screen printing of silver conductive paste (see Fig. 2a–b). The prepared graphene–PEDOT:PSS solution was then inkjet-printed over a rectangular electrode area of 1.5 × 2.5 cm2 using modified HP deskjet 2000 j210 printer with a resolution (BW) of 1200 × 1200 dpi (see Fig. 2b). The original ink in a printer cartridge was removed. The printer cartridge was thoroughly rinsed with DI water, dried with nitrogen gas and refilled with the prepared electronic ink. The thickness of inkjet-printed film could be controlled by varying the number of printed layers. It was found that the thickness of inkjet-printed film measured by a stylus profilier (DektakXT, Bruker Corp.) increases approximately linearly with the number of printed layers (see Fig. 5 in the Supplementary information). The pristine PEDOT/PSS gas sensor was also fabricated and tested as a reference for comparison. The fabricated flexible graphene–PEDOT:PSS gas sensor is displayed in Fig. 2c–d. The thicknesses of pristine PEDOT:PSS and graphene–PEDOT:PSS sensing films with 8 printed layers are ~402 nm and ~407 nm, respectively.
2.3. Gas sensing measurement

The sensor resistances were measured in a borosilicate glass chamber at a constant applied voltage (10 V) using a simple voltage divider circuit. The volume of the chamber was 15 l. The response and selectivity of the sensors were then assessed by the standard flow-through method towards ethanol, methanol, toluene, acetone, diethylamine and NH\textsubscript{3} with gas concentrations ranging from 5 ppm to 1000 ppm at room temperature. A constant flux of synthetic air of 2 l/min was mixed with the target gas source at different flow rate ratios to desired concentrations using mass flow controllers. All experiments were performed at room temperature (26 ± 2 °C) and the relative humidity of 56 ± 2%. In addition, the sensors were tested for flexible operation by bending to various degrees under exposure to NH\textsubscript{3} pulses. The bending angle was measured using a goniometer. The data were recorded every second using LabVIEW via a USB DAQ device for subsequent analyses.

3. Results and discussion

3.1. Characterization of sensing films

Surface morphologies and phase images of printed PEDOT:PSS and graphene–PEDOT:PSS sensing films were characterized by atomic force microscopy (AFM) with tapping mode as shown in Fig. 3. From AFM images, it can be seen that pristine PEDOT:PSS film surface is very smooth containing only few tiny defects over a scan area of 10 \(\mu\text{m} \times 10 \mu\text{m}\) (see Fig. 3a). With graphene inclusion, the film surface becomes relatively rough covering with a number of nanoprotrusions (see Fig. 3b). The nanoprotrusions have polygonal shapes with varying dimension in the range of \(\sim 50–1500 \text{nm}\) and hence should be corresponding to graphene nanosheets randomly embedded in PEDOT:PSS matrix. The average surface roughness of PEDOT:PSS and graphene–PEDOT:PSS are estimated to be \(\sim 2.73 \text{nm}\) and \(\sim 27.82 \text{nm}\), respectively. The much larger surface roughness of graphene–PEDOT:PSS film suggests a significant enhancement of the active surface-area for gas adsorption by graphene [24]. From the AFM phase image (see Fig. 3c), the PEDOT:PSS sensing film shows relatively low contrast in the phase (0–20°). The bright and dark areas in the phase image are expected to correspond to PEDOT-rich grains and PSS-rich matrix, respectively. It is seen that the grain and matrix mixture is homogeneous indicating that PEDOT-rich grains exhibit very good connection with PSS-rich matrix via EG and DMSO binders resulting in the enhancement of carriers conducting pathways [25]. In case of graphene–PEDOT:PSS (see Fig. 3d), the strong contrast in the phase (0–52°) can
distinguish the relatively hard structures (graphene) from the softer component (PEDOT:PSS). However, the graphene structures in and on PEDOT:PSS network cannot be very clearly distinguished due to overcoating of PEDOT:PSS on graphene surfaces and limited resolution in AFM.

The detailed structures of graphene dispersed in DMSO and PEDOT:PSS solutions were examined by transmission electron microscopy (TEM) as displayed in Fig. 4. Fig. 4a shows a typical high resolution TEM image of the exfoliated graphene sheet in DMSO. It clearly shows well dispersed graphene sheets with 3–6 lattice fringes of sp²-bonded carbon structures. The result confirms that DMSO allows good graphene dispersion without affecting the quality of graphene structure. After mixing graphene into PEDOT:PSS, it can be seen that polygonal sheets are spreading over each other and they are covered with smooth material so that lattice fringes are invisible as shown in Fig. 4b. The polygonal sheets are additionally confirmed to be graphene by selected area electron diffraction (SAED) as shown in the inset of Fig. 4b. The electron diffraction spots are clearly visible and can be matched to that of standard crystal graphite [9,26]. The TEM and AFM results suggest that graphene dispersion without affecting the quality of graphene structure. After mixing graphene into PEDOT:PSS, it can be seen that polygonal sheets are spreading over each other and they are covered with smooth material so that lattice fringes are invisible as shown in Fig. 4b. The polygonal sheets are additionally confirmed to be graphene by selected area electron diffraction (SAED) as shown in the inset of Fig. 4b. The electron diffraction spots are clearly visible and can be matched to that of standard crystal graphite [9,26]. The TEM and AFM results suggest that graphene and PEDOT:PSS are formed into intercalated composite structures [27,28]. The graphene sheets are randomly embedded in PEDOT:PSS polymer matrix. PEDOT:PSS is coated on graphene surfaces and its single extended polymer chain can be intercalated between graphene layers leading to hybrid multilayer morphology.

Raman spectra of PEDOT:PSS and graphene–PEDOT:PSS sensing films are shown in Fig. 5. The characteristic peaks of PEDOT:PSS at 1116, 1418, and 1500 cm⁻¹ are attributed to C—O—C deformation vibration, C_a=C_b symmetric stretching vibration, and asymmetrical stretching vibration of PEDOT:PSS chain structure, respectively [29–32]. In case of graphene–PEDOT:PSS sensing film, carbon characteristic peaks at ~1335 cm⁻¹ (D band), ~1574 cm⁻¹ (G band) and ~2666 cm⁻¹ (2D band) are pronounced while PEDOT:PSS peaks are almost vanished. The disappearance of PEDOT:PSS designates the presence of π–π interactions between graphene and PEDOT:PSS and the loss of coil conformation in PEDOT:PSS chain structure [27]. The D peak represents either edge or lattice defects while the G peak corresponds to primary sp²-hybridized carbon bonds in graphene. The 2D band of graphene–PEDOT:PSS sensing film is related to zone boundary defects in graphene and can be used to indicate the number of sp² layers of graphene. The relatively broad 2D band of graphene compared with G band indicates that the existing graphene has a few sp² layers [33,34] corresponding to the TEM results.

FTIR spectra of inkjet-printed graphene, PEDOT:PSS and graphene–PEDOT:PSS sensing films are illustrated in Fig. 6. In the FTIR spectrum of graphene, the peaks at 1095, 1224, 1338, 1412 and 1713 cm⁻¹ are attributed to C—O stretching, C—OH stretching, C—C stretching, O—H deformation and C=O in the carboxyl stretching vibration modes, respectively [35–39]. The result suggests that the graphene contains carboxylic acid, carbonyl moieties and hydroxyl functional groups after treatment in DMSO as depicted in the schematic structure of functionalized graphene in Fig. 1a. In case of the spectra of PEDOT:PSS and graphene–PEDOT:PSS sensing films, they similarly contain peaks of S—phenyl bond in sulfonic acid at 1010, 1039,
and 1060 cm⁻¹, C=O stretching vibration peak at 1263 cm⁻¹ and C=S bond in the thiophene ring at 705, 858, and 946 cm⁻¹ [9,40]. In addition, C=C stretching vibrations peak of the thiophene ring at 1521 cm⁻¹ and C=O bonding peak at 1126 cm⁻¹ for PEDOT:PSS are slightly shifted to 1519 cm⁻¹ and 1120 cm⁻¹ for graphene–PEDOT:PSS. The small red shift in FTIR spectra of graphene–PEDOT:PSS sensing film could be due to the delocalization of electrons from aromatic rings and C=O bonds to the π-clouds of graphene [41]. This suggests the presence of π–π interactions between graphene and PEDOT:PSS. The π network exists in both graphene and PEDOT:PSS. When graphene is embedded in PEDOT:PSS matrix, PEDOT:PSS polymer chains can thus adsorb to the surface of the graphene via π–π interactions between both networks and its single extended polymer chains with linear or expanded-coil conformation can be intercalated between graphene layers. Moreover, graphene–PEDOT:PSS exhibits an extra C=O carbonyl stretching peak at 1743 cm⁻¹, indicating the successful formation of hybridized graphene–PEDOT:PSS sensing film [42].

The UV–visible spectrometry (Lambda 650, Perkin Elmer) was used to verify the π–π transitions in graphene and PEDOT:PSS as shown in Fig. 7. A broad absorption band (centered at ~268 nm) of graphene is attributed to the π–π transitions of aromatic C=C bonds [43]. In case of PEDOT:PSS, the UV–visible absorption spectrum exhibits two peaks at 254 nm and 260 nm corresponding to typical absorption bands of the aromatic rings in PSS [44]. In case of graphene–PEDOT:PSS composite, the absorption peaks of PSS aromatic rings are red-shifted and superimposed on the broad absorption band of graphene. These results suggest the blending of graphene in the PEDOT:PSS composite and π–π electron donor–acceptor interaction between graphene and PEDOT:PSS [45].

3.2. Gas sensing properties

Fig. 8 shows the dynamic responses of the flexible printed PEDOT:PSS and graphene–PEDOT:PSS gas sensors towards 500 ppm NH₃ at room temperature. It indicates that the sensor exhibits good repeatability of response towards repeated NH₃-sensing cycles at room temperature. The resistances of both sensors increase upon exposure to NH₃ and recover to the initial value upon the removal of NH₃ in air. The resistance changing behaviors may be attributed to the adsorption and desorption of NH₃ molecules of the sensing films. The details of sensing mechanism for graphene–PEDOT:PSS gas sensor will be discussed in the next section. In addition, it can be observed that graphene–PEDOT:PSS gas sensor has much lower initial resistance than pristine PEDOT:PSS. The conductivities of PEDOT:PSS (~402 nm thick) and graphene–PEDOT:PSS (~407 nm thick) sensing films measured by
Fig. 4. (a) High-resolution TEM image of graphene in DMSO and (b) typical bright field TEM image of graphene–PEDOT:PSS nanocomposite.

Fig. 5. Raman spectra of (a) graphene–PEDOT:PSS and (b) PEDOT:PSS sensing films.

Fig. 6. FTIR spectra of graphene, PEDOT:PSS and graphene–PEDOT:PSS sensing films.

Fig. 7. UV–visible spectra of graphene, PEDOT:PSS and graphene–PEDOT:PSS composite.

Fig. 8. Dynamic responses of the flexible printed PEDOT:PSS and graphene–PEDOT:PSS gas sensors to 500 ppm NH₃ at room temperature.
4-point probe technique at 10 nA applied current are $0.790 \times 10^2 \text{Sm}^{-1}$ and $1.755 \times 10^2 \text{Sm}^{-1}$, respectively. It corresponds to a significant increase of charge carrier concentration due to graphene incorporation. From the results, the conductivity of PEDOT:PSS is increased by more than a factor of two after 2.33 wt.% graphene addition. Thus, graphene plays a dominant role in the charge transport through the PEDOT:PSS matrix. Graphene with a high conductivity of $7.813 \times 10^3 \text{Sm}^{-1}$ (reported by Cheap Tubes Inc.) may form conduction channels that substantially enhance the charge transport process.

The response time, defined as the time to reach 90% of the maximum total resistance change, of the flexible printed PEDOT:PSS and graphene–PEDOT:PSS gas sensors are estimated to be ~6 min and ~3 min, respectively. Moreover, the resistance of graphene–PEDOT:PSS gas sensor could recover almost completely to the initial value within the pure air exposure times of 5 min while the PEDOT:PSS gas sensor shows undesirable resistance drift. Thus, graphene–PEDOT:PSS gas sensor exhibits relatively short response and recovery times compared with PEDOT:PSS one. The slower response and recovery of PEDOT:PSS gas sensor may be due to low diffusion and short penetration depth of gas molecules on very smooth surface of the PEDOT:PSS sensing film.

In order to investigate the response and selectivity of flexible printed PEDOT:PSS and graphene–PEDOT:PSS gas sensors, they were exposed to a variety of volatile organic compounds (VOCs) including NH$_3$, diethylamine, acetone, ethanol, methanol and toluene at concentrations ranging from 5 ppm to 1000 ppm at room temperature. The response characteristic is then analyzed from the percentage change of the gas response defined as $S(\%) = \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \times 100$, where $R_{\text{air}}$ and $R_{\text{gas}}$ are the sensor resistance in pure air and in test gas, respectively. Fig. 9 demonstrates the gas response of PEDOT:PSS and graphene–PEDOT:PSS sensors as function of gas concentration of various VOCs. It can be seen that the flexible pristine PEDOT:PSS sensor shows relatively high response to NH$_3$ compared with diethylamine, acetone, ethanol, toluene and methanol at room temperature (Fig 9a). At 1000 ppm concentration, the gas response of PEDOT:PSS sensor to NH$_3$, diethylamine, ethanol, acetone, toluene and methanol are 6.9%, 5.9%, 3.2%, 2.8%, 2.1% and 1.9%, respectively. At low concentration (5–50 ppm), PEDOT:PSS is still able to respond to NH$_3$ with gas response ranging from 0.9–3.7% (inset of Fig. 9a).

With graphene addition, the gas response and selectivity to NH$_3$ are substantially improved as seen in Fig. 9b. The graphene–PEDOT:PSS gas sensor exhibits a remarkably high response to NH$_3$ but is almost insensitive to acetone, ethanol, toluene and methanol over the concentration range of 5–1000 ppm. The gas responses towards 500 ppm NH$_3$ of graphene–PEDOT:PSS, PEDOT:PSS and pristine graphene gas sensors are calculated to be 9.6%, 4.4% and 2.4%, respectively (see also Fig. S2 in the Supplementary information). It is seen that the room temperature response of pristine graphene to NH$_3$ is much lower than that of pristine PEDOT:PSS but the response is substantially enhanced after graphene inclusion. Thus, graphene enhances NH$_3$ interaction leading the higher charge reduction only when it is included in PEDOT:PSS network. At 1000 ppm of NH$_3$, the gas response of graphene–PEDOT:PSS sensor increases further to 18.9% which is almost 3 times as high as that of PEDOT:PSS gas sensor. At low concentration (5–50 ppm), the gas response of graphene–PEDOT:PSS gas sensor to NH$_3$ is still higher than that of undoped one with the gas response ranging from 1.2% to 5.5% (inset of Fig. 9b). However, the gas response of graphene–PEDOT:PSS sensor to NH$_3$ and diethylamine are not significant different in the low concentration range (5–10 ppm). The detection limit of NH$_3$ for graphene–PEDOT:PSS sensor is thus estimated to be less than 10 ppm at the room temperature. It should be noted that the NH$_3$ and diethylamine have the similar amines functional group that has electron lone pairs. Therefore, the relatively low response to diethylamine demonstrates that graphene–PEDOT:PSS gas sensor exhibits good NH$_3$ selectivity to other similar gas at concentration >25 ppm. Moreover, the stability of flexible printed graphene–PEDOT:PSS gas sensor has been assessed with exposure to 500 ppm NH$_3$ every week for 6 months under room-temperature storage at a relative humidity of 56 ± 5%. The sensor shows good medium-term stability up to 3 months with only ~12% of response reduction from its original response (see Fig. S3 in the Supplementary information). However, the response begins to degrade considerably afterward and the best usage time of the sensor under ambient storage is around 3 months.

The enhanced NH$_3$ sensing properties of graphene–PEDOT:PSS gas sensor may be attributed to (I) the increase of the surface roughness as shown in Fig. 3, (II) intrinsic sensing properties of graphene and (III) π-electron interaction by graphene loading in sensing film. (I) The gas sensitivity is directly proportional with the surface roughness of sensing film due to provide a specific surface-to-volume ratio [46]. The much larger surface roughness of graphene–PEDOT:PSS film therefore enhances the active surface area for gas adsorption. (II) It is well-known that graphene under ambient conditions behaves as p-type semiconductor that contains hole-like charge carriers [47]. When graphene-based sensor is exposed to an electron donating gas like NH$_3$, depletion of holes from the valence band of graphene occurs resulting in a significant increase in resistance. Thus, the addition of graphene in PEDOT:PSS leads to the increase of NH$_3$ response. (III) NH$_3$ molecules may interact with not only graphene and PEDOT:PSS but also π–π bonding between graphene and PEDOT:PSS [48]. Under the exposure to polar molecules like NH$_3$, the interaction can induce charge-transfer across delocalized π-electrons resulting in the improved sensing performances. To further verify the role of graphene in PEDOT:PSS, the sensor response was studied with varying graphene content from 0.12 to 2.33 wt.% (see Fig. S4 in the Supplementary information). It is found that the gas response to 500 ppm NH$_3$ at room temperature increases monotonically with increasing graphene content and further increase of graphene content tends to yield higher response. The higher graphene content will lead to an increase of π network, conjugation length in polymer matrix and π–π interaction. Thus, the result suggests that π–π interaction may play an important role in the response
enhancement. It should be noted that the graphene content has been limited to 2.33 wt.% due to printer-head clogging and inhomogeneous sensing-film problems.

The effect of bending on NH$_3$ sensing of graphene–PEDOT:PSS and PEDOT:PSS sensors was investigated by varying the bending angle ($\theta$) from 10$^\circ$ to 70$^\circ$ under exposure to 500 ppm NH$_3$ as shown in Fig. 10. Response deviation ($\Delta S$) is defined as $\Delta S = S_h - S_0$, where $S_h$ and $S_0$ are the gas response of sensor with bending angle ($\theta$) and zero bending angle, respectively. It is interesting that the gas response to NH$_3$ of both sensors increases as the bending angle increases. At bending angle of 70$^\circ$, the responses to 500 ppm NH$_3$ of graphene–PEDOT:PSS and PEDOT:PSS sensors increase from 9.6% to 15.8% (+6.2%) and from 4.4% to 9.7% (+5.3%), respectively. The increased NH$_3$ sensing response by bending angle may be attributed to the enhanced swelling process, in which NH$_3$ molecules can easily diffuse into the graphene–polymer layer under bending extension.

3.3. Sensing mechanism of graphene–PEDOT:PSS sensor

Several sensing mechanisms have been proposed for the conducting polymer systems including redox reactions between the polymer and analyte, charge transfer between the polymer and analyte and polymer swelling [49,50]. In
In this case, the resistance of graphene–PEDOT:PSS increases upon NH₃ exposure and decreases to its initial based line in pure air. This resistance changing behavior may be explained based on three possible mechanisms:

(I) Reducing reaction between NH₃ and chemisorbed oxygen (O₂(ads) + e⁻ → O₂(ads)) on the p-type graphene–PEDOT:PSS surface. It is known that O₂ is the predominant chemisorbed oxygen species on some active materials at low-temperature (<100 °C) [51]. O₂ may be trapped at the surface of graphene–PEDOT:PSS sensing film in dry air before NH₃ exposure. When NH₃ molecules directly adsorb on the surface, it reacts with the oxygen species and gives electrons back to graphene–PEDOT:PSS surface according to the reaction: 4NH₃(gas) + 5O₂(ads) → 4NO(gas) + 6H₂O(gas) + 5e⁻ [52]. The transferred electrons in conduction band recombine with holes from valence band resulting in lower carrier concentrations and higher resistance of the p-type graphene–PEDOT:PSS sensing film. However, chemisorbed oxygen should be less dominant in the sensing mechanism of graphene–PEDOT:PSS film since the concentration of O₂ should be very low at room temperature.

(II) Direct charge transfer process between NH₃ molecules and graphene–PEDOT:PSS surface. When NH₃ molecules are adsorbed on the graphene–PEDOT:PSS surface by physisorption, the holes of conductive graphene–PEDOT:PSS will interact with the electron-donating NH₃ analyte [53]. The delocalization degree of conjugated π electrons of sensing film is increased by charge transfer from the adsorbed NH₃ molecules. This leads to the formation of a neutral polymer backbone and decrease in charge carriers resulting in the decrease of the electrical conductivity of the sensing film [54,55]. This mechanism is widely adopted for explanation of the change in conductivity of conductive polymer to acidic/basic analytes (doping/dedoping process).

Moreover, the addition of graphene into PEDOT:PSS increases specific adsorption surface area and π–π interactions leading to improved sensing performances of the flexible gas sensor.

(III) Swelling process from the diffusion of NH₃ molecules into the graphene/polymer chains matrix. In PEDOT:PSS sensing films, a single PSS chain interacts electrostatically over its length with many shorter PEDOT chains, which tend to have short interchain distance [56]. Thus, the electron hopping process prefers to occur between PEDOT chains. When NH₃ molecules diffuse into polymer matrix, electron hopping process becomes more difficult because the PEDOT interchain distance increases due to the swelling process. In the case of graphene–PEDOT:PSS sensor, graphene embedded into polymer matrix acts as conductive pathways that favor the hopping of electrons. The swelling process can cause the graphene to stay apart, disrupting conductive pathways in the sensing film. The increase of PEDOT distance and decrease of graphene’s conductive pathways occur simultaneously, leading to significant increase in resistance of the graphene–PEDOT:PSS sensor upon NH₃ exposure and therefore enhanced NH₃ response. The resistance of graphene–PEDOT:PSS sensor will recover to its base line after polymer shrinks back into the initial volume by NH₃ out-diffusion via the purge of dry air.

Based on the results, direct charge transfer process appears to be the most probable dominant process for NH₃-sensing of the graphene–PEDOT:PSS sensor due to the observed high response and selectively to polar molecules. Moreover, the sensors show very low response to humidity, which normally causes considerable response in polymer-based gas sensor operating based on swelling mechanism. Furthermore, the graphene–PEDOT:PSS sensor exhibits relatively fast dynamic response with almost full recovery in relatively short desorption time compared with other sensors at room temperature when physisorption is dominant over chemisorption.

4. Conclusion

The flexible PEDOT:PSS and graphene–PEDOT:PSS gas sensors have been successfully fabricated by ink-jet printing technique and characterized for NH₃ sensing. AFM, TEM, FTIR, UV–visible spectra and Raman characterizations confirm the presence of few-layer graphene in PEDOT:PSS polymer matrix and π–π interactions between graphene and PEDOT:PSS. The incorporation of graphene in PEDOT:PSS leads to considerable enhancement of NH₃ response, dynamic behavior and selectivity to NH₃ due possibly to the increase of the specific surface area, intrinsic sensing properties of graphene, and π–π interaction in graphene–PEDOT:PSS. The flexible graphene–PEDOT:PSS gas sensor exhibits high sensing performance to NH₃ with concentrations ranging from 25 to 1000 ppm at room temperature. In addition, the gas response considerably increases with increasing the bending angle. Reducing reaction with
chemisorbed oxygen, direct charge transfers and swelling process are among possible sensing mechanisms of the flexible printed graphene–PEDOT:PSS sensor. Detailed analysis indicates that the most dominant contribution seems to be the direct charge transfer while chemisorbed oxygen is the least possible mechanism. From the results, the proposed technique offers several distinct advantages over some other methods including high sensing performances, low temperature processing, high productivity, simplicity and low cost. Moreover, it will be useful for development of future wearable electronic technology.

Acknowledgments

This work was financially supported by Kasetsart University Research and Development Institute (KURDI), Y.S. acknowledges M.Sc. Scholarship for International Publication from the Graduate School, Kasetsart University. T.K. expresses his gratitude to Mahidol University.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orgel.2014.08.044.

References


