Ammonia Gas Sensing Characteristic of P3HT-rGO-MWCNT Composite Films

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Abstract: In this work, the P3HT:rGO:MWCNTs (PGC) nanocomposite film applied to the ammonia gas sensor was successfully fabricated by a drop-casting technique. The results demonstrated that the optimum weight ratio of the PGC nanocomposite gas sensor is 20%:60%:20% as the weight ratio of P3HT:rGO:MWCNTs (called PGC-60). This weight ratio leads to the formation of nanostructured composites, causing the efficient adsorption/desorption of ammonia gas in/out of the film surface. The sensor based on PGC-60 possessed a response time of 30 s, sensitivity up to 3.6% at ammonia gas concentration of 10 ppm, and relative sensitivity of 0.031%/ppm. These results could be attributed to excellent electron transportation of rGO, the main adsorption activator to NH$_3$ gas of P3HT, and holes move from P3HT to the cathodes, which works as charge “nano-bridges” carriers of Multi-Walled Carbon Nanotubes (MWCNTs). In general, these three components of PGC sensors have significantly contributed to the improvement of both the sensitivity and response time in the NH$_3$ gas sensor.

Keywords: P3HT-rGO-MWCNT nanocomposite; drop-casting; heterojunction; NH$_3$ gas sensors; response time; sensitivity

1. Introduction

Ammonia (NH$_3$) significantly contributes to the nutritional requirements of terrestrial organisms by acting as a precursor to foods and fertilizers. However, with an exceptionally large concentration, ammonia gas will be a toxic compound and harmful to humans and other species [1]. Because of rapid industrial development, ammonia gas has been released into the environment in excessive amounts and without restriction. Therefore, developing sensitivity, selectivity, and stability of devices/sensors to detect ammonia gas is an important task in this day and age. Gas sensors based on inorganic nanostructures such as TiO$_2$, SnO$_2$, WO$_3$, etc. show high response time and sensitivity. However, they are typically fabricated under high vacuum and temperature conditions which results in significantly high production costs [2]. To reduce production costs, a conductive polymer-based gas sensor has been developed [3–9]. The advantages of polymer-based sensors are the low power consumption, simple fabrication process, and room temperature operation [10]. Among conductive polymers, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) is usually utilized in optoelectronic components such as organic solar cells (OSC) and organic light-emitting diodes (OLED). PEDOT: PSS is known as a good candidate for gas sensors detecting CO [11], NH$_3$ [12], and vapors of organic solvents or water [13,14]. It is shown that, by controlling the degree of reduction, the bandgap of
reduced graphene oxide (rGO) can be adjusted from 1.00 to 1.70 eV [15–18]. Abid et al. [19] prepared rGO-based films using the Hummers technique for wideband optical sensors and Seekaew et al. [20] fabricated the ultra-high selective NH₃ gas sensor based on the nanocomposite Sn/TiO₂-rGO-CNTs by the solvothermal method. The variation in a component of the NH₃ composite sensor was explained by the p-n heterojunction, which was built by p-type materials such as rGO/CNT nanoparticles and n-type materials such as Sn-TiO₂ nanoparticles, etc. The novel gas sensor, able to detect NH₃ at room temperature, based on the Pd/SnO₂/rGO film, was fabricated by the one-pot route method [21]. Zhang et al. [22] demonstrated that the NH₃ wireless sensors which operate at room temperature with a response time of 7.5 s and a recovery time of 20 s in an NH₃ concentration ranging from 5 to 100 ppm can be made from Ag-rGO composite films. Moreover, the electrical properties of multi-wall carbon nano tubes (MWCNTs) are a critical function of their atomic structure—any mechanical strain or chemical doping can cause large changes in electrical conductivity [23]. Therefore, to overcome the limitations of semiconductor gas sensors, MWCNT-based gas sensor has been fabricated for high gas adsorption capacity and small size, i.e., the advantages of MWCNTs. MWCNTs are expected to be an economically viable material for use in gas detection. For these reasons, so far, MWCNTs have been explored to sense gases in a number of different configurations [24].

Sensors based on PEDOT: PSS can detect both ammonia gas [25] and humidity are recently reported by Lam Minh Long et al. [26] where PEDOT: PSS+rGO+AgNWs-based sensors have good sensitivity and are sensitive to relative humidity (RH). For practical applications, a sensor should be able to detect gas with high sensitivity and selectivity. The OSCs study, which uses poly(3-hexylthiophene) (P3HT) as a photoactive layer [27], shows that the P3HT film exposed to air with a relative humidity greater than 60% gives good quality as that in a dried nitrogen glove box. This suggests that a combination of rGO, P3HT, and MWCNTs can be utilized in gas sensor fabrication to monitor atmospheric NH₃. Therefore, this work focused on the preparation of the P3HT-rGO-MWCNT composite film that sensors ammonia in the range of 10–90 ppm.

2. Experimental

2.1. Preparation of the Graphene Solution

Chemicals such as P3HT and multi-walled carbon nanotubes (MWCNT), with a purity of 99.99% were purchased from Sigma-Aldrich Ltd., product number: 755125-1G. Reduced graphene oxides (rGO) prepared by the modified Hummers method have been described in detail in previous reports [28–30]. In this study, 10 mg of rGO was dispersed in 10 mL of N,N-Dimethylformamide (DMF) solvent using the ultrasonic technique for 1 h to produce a bare rGO-DMF solution.

2.2. Preparation of the P3HT-rGO-MWCNT Blends

The P3HT-rGO-MWCNTs blends were prepared based on methods reported in ref. [31]. To be specific, P3HT powder was mixed in the rGO-DMF solution. The mixed solution was then ultrasonic stirred for 2 h at room temperature to produce P3HT-rGO-DMF solutions. The MWCNTs were immersed in the DMF and ultrasonic stirred for 1 h to form the MWCNT-DMF solution. Finally, the prepared P3HT-rGO-DMF and MWCNT-DMF solution was mixed in a small glass beaker and stirred for another 5 h at 80 °C. The mass ratio of the mixture P3HT:rGO:MWCNTs was changed at 10:80:10, 20:60:20, and 30:40:30, respectively, to evaluate the NH₃ gas detecting sensitivity of the sensor based on rGO content. To simplify, samples of the mixture P3HT:rGO:MWCNTs are abbreviated to PGC, where PGC-40, PGC-60, and PGC-80 are the samples with an rGO content of 40%, 60%, and 80%, respectively.

2.3. Fabrication of Gas Sensors NH₃ by the Drop-Casting Method

ITO grid electrodes (IGE) were prepared by masking and wet chemical etching processes, as shown in Figure 1. First, the IGE substrate was heated up to 150 °C. In the next
step, the prepared PGC solution was dropped onto the IGE, then dried for 5 min. The dried samples were then annealed in gaseous nitrogen at 180 °C for 45 min. Finally, the samples were annealed at 160 °C for 2 h in an “SPT-200” vacuum dryer. The thickness (d) of the PGC film was controlled by the amount of solution and the annealing time. In this experiment, the film thickness was kept at a constant of about 550 nm.

![Diagram](image)

**Figure 1.** The schematic draw of the drop-casting technique for preparing resistance sensors.

### 2.4. Characterization Techniques

The surface morphology, crystal structure, and optical absorption of the samples was characterized using a “Hitachi S-4800” field emission scanning electron microscope (FE-SEM), D5000 with CuKα1 radiation (λ = 1.5406 Å) and a UV-Vis spectrophotometer (Jasco, V-670), respectively. The technique reported by Long et al. [31] to monitor NH3 gas as described below was used in this study. The sensors were placed in a testing chamber with a volume of 10 dm³. By using the “EPA-2TH” prometer (USA), the chamber airflow can be precisely controlled (from 1 to 100 sccm) corresponding to an NH3 concentration ranging from 10 ppm to 90 ppm. The sensor’s gas sensitivity was assessed by the following steps: the sensor was placed in a test chamber at a temperature, pressure, and humidity of 300 K, 1 atm, and 10%, respectively; The 2400-Keithley power meter was used to determine the resistance between the two electrodes of the sensor. The sensor’s gas sensitivity was assessed through two adsorption and desorption processes. During adsorption, a gas stream (or vapor) consisting of the Ar carrier and the measured vapor was introduced into the test chamber for a period of time, and a change in the sensor resistance was recorded. During desorption, a stream of dry Ar gas was introduced into the chamber to restore the original resistance of the sensors. The sensitivity and desorption of the sensor can be assessed by the time-dependent change in resistance.

### 3. Results and Discussion

#### 3.1. Morphology and Structure of the Films

FESEM images of the synthesized rGO, MWCNTs, and PGC composite films were shown in Figure 2. In Figure 2a, the rGO layers are well separated from each other smooth surfaces. MWCNTs have an average diameter of about 25 nm and are also separated from P3HT layers (Figure 2b). These figures indicate that P3HT is able to be utilized as a smooth surface of the MWCNTs layer, especially when P3HT was mixed with rGO (Figure 2c). The presence of both rGO and MWCNTs resulted in the formation of multiple nanostructured heterostructures of rGr/P3HT and CNT/P3HT in the PGC films.
Figure 2. FE-SEM of (a) rGO made by the modified Hummers method, (b) MWCTs, and (c) P3HT-rGO-MWCNTs.

XRD characterization of the PGC film shows four peaks. Among them two distinctive peaks (002) and (101) belong to MWCNTs [32]; two other peaks are unidentified (Figure 3). The representative peak of rGO made by the modified Hummers method are immersed in the (002) peak of MWCNTs and obviously, a P3HT amorphous cluster dispersed in a rGO matrix did not exist in XRD pattern.

Figure 3. XRD pattern of the PGC-60 film.

3.2. UV-Vis Absorption Properties

Figure 4a shows the optical absorption spectra of the P3HT film and the PGC-60 composite film fabricated by the drop-casting method. It shows that the P3HT film strongly absorbs light in the range of wavelength from 400 nm to 600 nm. The strongest absorbance of the P3HT film (marked ‘1’ peak) is at 558 nm and is characterized by the $\pi-\pi^*$ bond in the P3HT series [33]. For PGC-60 composite films, two peaks are appearing in the optical absorption spectrum: the first one (namely peak ‘2’) is at about 514 nm and belongs to a blue shift of P3HT and the other peak is at 318 nm (peak ‘3’), which could be due to the presence of rGO with a moderate reduction [34]. It needs to be noted that the band gap of rGO is about 2.8 eV [35], which is much larger than the band gap of P3HT [36] and that the CNT embedded in P3HT causes no more additional peak. Furthermore, in comparison to the pure P3HT layer, the absorption of the PGC-60 composite films from 300 nm to 600 nm is much greater. This is the desired factor for a photoactive layer in polymeric composite solar cells, which was observed [27]. These advantages in electrical properties of the PGC composites due to the GQDs/P3HT heterojunctions and CNTs charge bridges are put into consideration in the preparation of our gas sensors with great sensitivity and selectivity in a humid environment.
Figure 4. (a) UV-Vis absorptance spectra and (b) plots of \((\alpha h \nu)^2\) vs. \(h \nu\) of drop-casting P3HT and PGC-60 composite films.

In this work, the UV-Vis spectra were used to estimate the bandgap energy \(E_g\) using the expression [37]:

\[
\alpha h \nu = A (h \nu - E_g)^n
\]  

(1)

where \(h\), \(n\), and \(A\) are the Planck constant, the frequency of the incident photon, and the constant of the expression, respectively. \(n\) has a value of 1/2 or 2 for a semiconductor with a direct or indirect bandgap, respectively. For both indirect bandgap samples P3HT and PGC, \(n\) is equal to 2. The dependence of \(h \nu\) on \((\alpha h \nu)^2\) of the samples were shown in Figure 4b. The calculated results show that the lines segments AB and CD exhibit the linear dependence of \(h \nu\) on \((\alpha h \nu)^2\). The x intercept of linear extrapolation of AB and CD give bandgap values of 1.92 eV (for P3HT) and 2.02 eV (for PGC), respectively. The calculated \(E_g\) value of P3HT (1.92 eV) is close to the \(E_g\) value reported by [29] where P3HT was prepared for hybrid solar cells. The increase in values of the bandgap of the synthetic films (from 2.02 eV for the pure P3HT to 1.92 eV for PGC-60 composite film) can be explained by the presence of both rGO and CNTs, which causes a reduction in the polymer’s chain length and leads to an expansion in the bandgap of the polymer [38].

3.3. Ammonia Gas Sensing of P3HT-Based Composite Films

According to the gas sensing principle, when a gas sensor contacts a certain gas (such as \(\text{NH}_3\), \(\text{NO}_x\), \(\text{H}_2\), etc.), its resistance changes. Depending on the nature of the material used (semiconductor oxides and/or composite film) and the measured gas, the resistance of the gas sensor will be decreased or increased. In this study, P3HT is considered as a p-type organic semiconductor [39], so when the sensor’s surface comes into contact with \(\text{NH}_3\) gas, the resistance of the PGC sensor will be increased due to the decrease in the number of holes in P3HT. When \(\text{NH}_3\) molecules are adsorbed on the sensor’s surface, electrons tend to recombine with holes, leading to a decrease in the primary carriers (holes), followed by increase in P3HT resistance. For the faster re-adsorption of \(\text{NH}_3\), the PGC sensors are heated at about 150 °C. The molecules of ammonia gas quickly left from the sensor surface, taking with them electrons from the above-coupled charge carriers. Therefore, holes will be regenerated in the P3HT polymer, resulting in the decrease of the sensor resistance.

In the study of the sensing properties of a resistance sensor, a performance parameter usually used is the sensitivity \(\eta\) that shows the difference (in percentage) between the initial resistance \(R_0\) and the resistance \(R\) of the sensor exposed in the monitored gas. Thus, \(\eta\) is expressed by the following equation:

\[
\eta = \frac{R - R_0}{R_0} \times 100(\%)
\]  

(2)
From experimental measurements of the response time of the sensor at a NH$_3$ gas concentration of 70 ppm, the adsorption/desorption time ($t$) dependence of the sensitivity of the PGC sensors is plotted in Figure 5, which consists of three $\eta$-$t$ curves corresponding to PGC-40, PGC-60, and PGC-80 devices. Figure 5 demonstrates the adsorption and desorption processes of the PGC-based sensors. This figure shows that in the first 50 s, Ar gaseous flow eliminated the contamination agents from the PGC surface; consequently the surface resistance of the sensor was not stable. After the cleaning of the sensor surface during 30 s, the introduced NH$_3$ was adsorbed onto the sensor surface, resulting in the increase in resistance. In the subsequent cycles, the NH$_3$ desorption/adsorption process led to decrease and increase of the resistance of sensors, respectively, with results similar to those reported in [40]. The best sensitivity of the device was found to be about 5.0%; desorption ability, especially, was 95% in the 60 s for the PGC-60 sensor where rGO content in the composite film is 60 wt.% (Figure 5b). In case the amount of rGO is lower in the PGC-40 sample, the accumulated P3HT chains become larger. On the opposite side, the larger amount of rGO in the PGC-80 device leads to the overlap of the rGO sheet on the P3HT chain. In both cases, their gas sensitivity and desorption capability of composite film decrease significantly (Figure 5a,c). Thus, the optimum content of rGO in the composite NH$_3$ gas sensor was found to be 60 wt%, corresponding to the weight ratio of P3HT:rGO:MWCNT equal to 20:60:20. A comparison of the sensor sensitivity caused by different active materials for NH$_3$ detection and the data obtained in this work are shown in Table 1.

![Figure 5](image_url)

Figure 5. (a–c) Sensitivity vs. rGO content in the PGC composite sensors, and (d) NH$_3$ gas sensitivity of pristine P3HT.
Table 1. PGC-60 ammonia sensor sensitivity in a comparison with literature data.

| Sensing Material   | NH3 Concentration (ppm) | Sensor Sensitivity (%) | Reference |
|--------------------|--------------------------|-------------------------|-----------|
| rGO+P3HT           | 50                       | 12.63                   | [41]      |
| SWCNT              | 500                      | 1.9                     | [42]      |
| rGO+TiO$_2$        | 30                       | 3.5                     | [43]      |
| polythiophene/    | 2000                     | 15                      | [23]      |
| MWCNTs            |                           |                         |           |
| PGC-60             | 10                       | 5                       | This work |

Figure 5 demonstrates that, compared to the use of the pristine P3HT polymer (Figure 5d, sensor sensitivity was significantly improved when using the rGO-MWCNTs-P3HT composite. Wang et al. also obtained similar results for sensors based on polypyrrole (Py)-rGO blends [44]. The improved sensitivity of the sensor based on the Py-rGO blend was attributed to the oxygen and structural defects after chemical reduction, which makes the rGO material act as a p-type semiconductor. Varghese et al. [45] also showed that the adsorption efficiency of gas molecules (including NH3) was improved through the use of MWCNTs resulting from the enlarging effective surface area. In addition, MWCNTs embedded in rGO can be thought of as “nano-bridges” for the transfer of charge carriers. In this work, these “nano-bridges” were clearly shown in the FE-SEM microscope image (Figure 2c). Furthermore, inorganic nanoparticles embedded in the polymer would fill up most of the cracked spots in the polymer that were usually created during the post-annealing process [27]. Consequently, in the nanocomposite films, the cracked spots that acted as the charged traps were eliminated. From the above analysis results, the improvement in the performance of the sensors made from PGC composite film was attributed to the heterojunction of P3HT/rGO, P3HT/CNT, and a reduction in the charged traps in the polymer film.

To clarify the role of rGO in the sensor, the sensors are based on P3HT-MWCNTs (without rGO), where the weight ratio of P3HT:MWCNT is 60:40 (abbreviated to P3C) were also fabricated. The sensitivity and relative sensitivity of the two types of devices were shown in Figure 6. The results showed that the response of the sensor linearly decreases with a decrease in ammonia gas concentration ($C$, ppm), and the slope of the linear plot reflects the relative sensitivity ($RS$) of the sensor. Thus, $RS$ can be determined by the following formula:

$$RS = \frac{\Delta \eta}{\Delta C} (\text{%/ppm})$$  

(3)

Figure 6. The (a) sensitivity and (b) relative sensitivity of P3HT-rGO-MWCNTs comparing to those of P3HT-MWCNTs sensors.
The result also indicated that the relative sensitivity of the P3C and PGC composite sensors was 0.012%/ppm and 0.031%/ppm, respectively. This clearly demonstrates that rGO played an important role in improving the performance parameters of sensors based on organic composites. Here, the relative sensitivity of the PGC sensor is about 2.5 times greater than that of the P3C sensor and about 1.5 times greater than that of the PEDOT:PSS sensor [46].

In summary, we would like to point out that in three-component composite sensors (namely P3HT, rGO, and MWCNTs), each component plays its specific and important role. While rGO is an excellent electron transporter, as pointed out in [47], a conducting polymer, P3HT, seen as a p-type organic semiconductor, is the adsorption activator to NH$_3$ gas. Owing to P3HT, electrons of NH$_3$ molecules are temporarily detached from their molecule. Then due to rGO, electrons move fast inside films and couple with holes in P3HT. Serving as charge carrier “nano-bridges”, MWCNTs favor holes transported from P3HT to the cathode of the device. In general, all three components in PGC sensors have significantly contributed to the improvement of both the sensitivity and response time in NH$_3$ gas sensing. The enhancement in charge transport during the performance of a composite-based NH$_3$ sensor can be explained by using the scheme of the energy levels, as shown in Figure 7.

![Figure 7](image-url)  
**Figure 7.** Scheme of the energy levels of single components of the PGC-60 composite sensor. The dashed arrows indicate hole movement directions during the resistance measurement.

4. Conclusions

The nanocomposite PGC sensors were successfully fabricated using the drop-casting technique. The sensitivity of the PGC gas sensor was optimized when the concentrations of P3HT, rGO, and MWCNTs were 20 wt.%, 60 wt.%, and 20 wt.% (PGC-60), respectively. The PGC-60 sensor has a response time of 30 s, sensitivity up to 3.6% at ammonia gas concentration of 10 ppm, and relative sensitivity of 0.031%/ppm. These results are attributed to excellent electron transportation of rGO, the adsorbent activator to NH$_3$ gas of P3HT, and holes move from P3HT to the cathodes as a charge carrier “nano-bridge” of MWCNTs. In general, all three components of the PGC sensor have significantly contributed to improving both the sensitivity and response time of the NH$_3$ gas sensor. The comparison of relative sensitivity of the PGC sensor to that of the P3C sensor and the PEDOT:PSS sensor is about 2.5 and 1.5 times greater, respectively.

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