

Graphene and Poly(Methyl Methacrylate) Composite Laminates on Flexible Substrates for Volatile Organic Compounds Detection

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Abstract

In this study, graphene and poly(methyl methacrylate) (GR/PMMA) composite laminates on flexible substrates were fabricated for the use in volatile organic compounds detection. The CVD-grown graphene on Cu foil was transferred on polyethylene terephthalate (PET) substrate by PMMA-assisted wet transfer process. Without PMMA removal, the GR/PMMA composite laminates on PET were obtained. Graphene and GR/PMMA sensors show completely different sensor response to VOC vapors. The resistance of graphene sensor decreases, while that of GR/PMMA increases upon VOC exposure. The graphene and GR/PMMA sensors show the highest magnitude of sensor response to dichloromethane. The sensor response of the GR/PMMA to acetone, chloroform and benzene are greatly suppressed, resulting in the selectivity improvement. The sensor response of graphene can be explained in terms of the dielectric constant of VOCs and electron hopping effects on defect graphene, while that of the GR/PMMA would be attributed to swelling mechanism.

1. Introduction

Recently, graphene, a perfect two-dimensional structure with a one layer of carbon atoms, have been interesting materials for gas sensor applications, due to its high charge mobility and thermal conductivity, high degree of transparency, as well as mechanical flexibility [1–2]. To use the chemical vapor deposition (CVD)-grown graphene on Cu foil for the device application, the polymer-assisted wet transfer process is employed to transfer graphene onto arbitrary substrate. However, graphene was degraded according to wrinkles, cracks and the residues of the metal and the supporting polymers during transfer process [3]. To overcome this problem, utilization of the graphene and supporting polymer composite and maximizing their property is a challenge [4–5].

In this research, to overcome the transfer issues and exploring the use of graphene and polymer composites to flexible device fabrication, graphene and poly(methyl methacrylate) composite laminates on polyethylene terephthalate (PET) substrates was fabricated for volatile organic compounds (VOC) detection.

2. Experimental method

The CVD-growth procedure of graphene on Cu foil was described elsewhere [6]. In preparing sensor on flexible substrate, graphene was transferred to PET by conventional PMMA-assisted wet transfer process. Briefly, PMMA (Microchem, 950PMMA A6) was spin-coated onto the graphene as a supporting layer with a spin speed of 6000 rpm for 300 s. The sample was then cured by heating on a hot plate at 100 °C for 24 hr. The Cu foil was etched away using a 1 M ferric (III) chloride solution. The sample was rinsed in deionized water for 10 min. Finally, the sample was transferred onto the PET substrate and dried at room temperature, resulting in transferred graphene and PMMA composite laminates on PET (hereafter referred to as GR/PMMA). Regarding sensor based on graphene, PMMA was removed by soaking in acetone at 150 °C for 5 min, followed by N₂ drying. The Ag paste with Cu wires were used as the contact electrodes for the sensing characterization with the sensing of 1x0.5 cm².

The sensor responses to VOCs (acetone, benzene, chloroform and dichloromethane (DCM)) were investigated at room temperature by recording the electrical resistance during cycles of alternating supply of dry N₂ gas and VOC vapor. The concentration of VOCs was in a range of 50 to 150 parts per thousand (ppt). The sensor response (*SR*) was defined as $SR = (R_{VOC} - R_0) / R_0$, where R_{VOC} and R_0 , are the resistances of the sensor after and before VOC exposure, respectively. To compare the responses of all sensors, the sensor responses were normalized by the VOC concentration. The normalized sensor response (*NSR*) was defined as the ratio between the sensor response at a time of 540 s (SR_{540}) and the VOC concentration (C_{VOC}) as $NSR = SR_{540} / C_{VOC}$.

3. Results and Discussion

Fig. 1a-1b show sensor responses as a function of time of the graphene and GR/PMMA sensors under alternating supply of N₂ gas and VOC vapor, respectively. The results show that the resistance of graphene sensor decreased upon VOCs

exposure and increased after recovery with N₂ gas. Meanwhile, the resistance of the GR/PMMA increased and decreased upon VOC exposure and after replacing VOC with N₂ gas, respectively. Fig. 1c shows the normalized sensor response of graphene and GR/PMMA sensor to VOC vapors. The order of the sensor response magnitude of graphene sensors is in the following order: DCM > chloroform > acetone > benzene, while that of the GR/PMMA is in the following order: DCM >> acetone > chloroform > benzene. Interestingly, the sensor response of the GR/PMMA sensors to DCM significantly increased, while those to acetone, chloroform and benzene were mostly suppressed. These results imply that the PMMA layer acts as a membrane to select VOC molecules, resulting in the selectivity improvement [7].

The sensing mechanism of the graphene to VOCs is attributed to the adsorption of VOC molecule on the defect site. Charge transfer on graphene by electron hopping effects on graphene sheet results in a decrease in electrical resistance of graphene [8]. For the GR/PMMA, the sensing mechanism can be ascribed to polymer swelling due to VOC adsorption and Hansen solubility parameter (HSP). A hypothesis based on polymer swelling can be described as follows. After VOC adsorption, polymer coatings on graphene is swollen, thus possibly increasing the polymer volume and bending of graphene sheet, resulting in an increase in electrical resistance [9]. The higher solubility, the larger magnitude of sensor response. The solubility of the vapors in PMMA is in the following order: DCM >> acetone > chloroform > benzene [10], which coincides with the sensor response. Moreover, the difficulty of the GR/PMMA to recover to baseline after DCM exposure indicates the high solubility of DCM.

3. Conclusions

In summary, we successfully fabricated graphene and PMMA composite laminates on PET substrate for the use in VOC detection. The graphene and GR/PMMA sensors show the highest magnitude of sensor response to dichloromethane in the opposite signal. The sensor response of the GR/PMMA to acetone, chloroform and benzene are greatly suppressed, resulting in the selectivity improvement. These preliminary results show the potential use of the graphene and GR/PMMA array for VOC discrimination

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References

- [1] S. M. Kanan, O. M. El-Kadri, I. A. Abu-Yousef, and M. C. Kanan, *Sensors* **9** (2009) 8158–8196.
- [2] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau, *Nano Lett.* **8** (2008) 902–907.
- [3] G. B. Barin, Y. Song, I. F. Gimenez, A. G. S. Filho, L. S. Barreto, J. Kong, *Carbon* **84** (2015) 82–90.
- [4] P. Y. Teng, C. C. Lu, K. Akiyama-Hasegawa, Y. C. Lin, C. H. Yeh, K. Suenaga, and P. W. Chiu, *Nano Lett.* **12** (2012) 1379–1384.

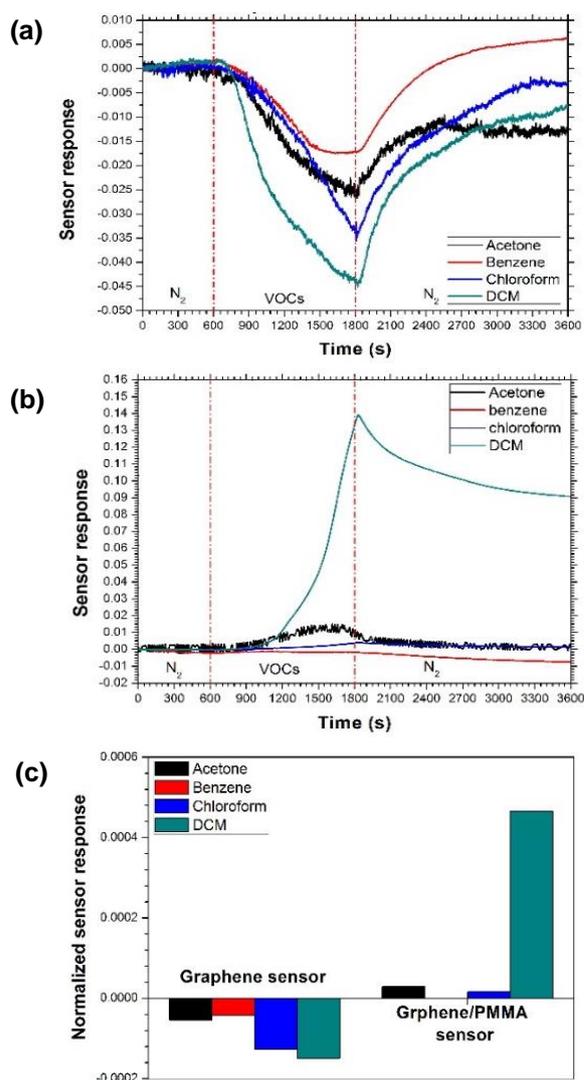


Fig. 1 Sensor responses to acetone (477.55 ppt), chloroform (253.97 ppt), dichloromethane (300.96 ppt) and benzene (295.90 ppt) as functions of time: (a) graphene and (b) GR/PMMA. (c) Normalized sensor response of graphene and GR/PMMA sensor to VOC vapors

- [5] I. Vlasiouk, G. Polizos, R. Cooper, I. Ivanov, J. K. Keum, F. Paulauskas, P. Datskos, and S. Smirnov, *ACS Appl. Mater. Interfaces* **7** (2015) 10702–10709.
- [6] Q. Wu, S.J. Jung, S.K. Jang, J. Lee, I. Jeon, H. Suh, Y.H. Kim, Y.H. Lee, S. Lee, Y.J. Song, *Nanoscale* **7** (2015) 10357–10361.
- [7] J. Hong, S. Lee, J. Seo, S. Pyo, J. Kim, and T. Lee, *ACS Appl. Mater. Interfaces* **7** (2015) 3554–3561.
- [8] G. Lee, G. Yang, A. Cho, J.W. Han, J. Kim, *Phys. Chem. Chem. Phys.* **18** (2016) 14198–14204.
- [9] W. Muangrat, T. Chodjarusawad, R. Maolanon, S. Pratontep, S. Porntheeraphat, W. Wongwiriyan, *Jpn. J. Appl. Phys.* **55** (2016) 02BD04.
- [10] C.M. Hansen, *The three dimensional solubility parameter and solvent diffusion coefficient: Their importance in surface coating formulation*, Danish Technical Press, (1967).