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Using Aligned P3HT/PMMA Fibers to Detect Volatile Organic Compounds

Shun-Hsiang Chan[1], Ming-Chung Wu[1,*] Shih-Hsuan Chen[1], Wei-Fang Su[2] and Chao-Sung Lai[3]

[1] Chang Gung Univ.
Department of Chemical and Materials Engineering
No.259, Wenhua 1st Rd., Guishan Dist., Taoyuan City 33302, Taiwan
Phone: +886-3-2118800 #3545 E-mail: mingchungwu@mail.cgu.edu.tw
[2] National Taiwan Univ.
Department of Materials Science and Engineering
No. 1, Sec. 4, Roosevelt Rd., Taipei 10617, Taiwan
[3] Chang Gung Univ.
Department of Electronic Engineering
No.259, Wenhua 1st Rd., Guishan Dist., Taoyuan City 33302, Taiwan

Abstract

Real-time and low cost detection of volatile organic compounds (VOCs) has raised a lot of interests for its capability of avoiding environmental disasters and also ensuring the safety of human health. The specific area of sensing materials affects the sensitivity of VOCs detectors significantly; therefore many techniques have been adopted to increase the specific surface of sensing materials to form the nanostructured materials. In this study, we fabricated a VOCs sensing chip consisting of random and aligned P3HT/PMMA fibers by the electrospinning technique. For detection principle of our VOCs sensing chip, it adopted the proposed methodology that the optical property of P3HT/PMMA blend is sensitive to VOCs vapor due to the morphological evolution and P3HT polymer structure, so that it can act as an indicator of the existence of VOCs. Preparation of aligned fibers can increase the sensitivity of the sensor chip.

1. Introduction

Volatile organic compounds (VOCs) are typically dangerous hazardous. When VOCs concentration is higher than the limits explosion, it leads to the explosions and fire accidents which result in serious injuries and deaths. Low cost, real-time detection of VOCs is really important that it can avoid environmental disasters and also ensure the safety of human health and properties. VOCs sensors are the imperative technology of modern life for environmental monitoring. The sensitivity of VOCs sensors is deeply affected by the surface area of sensing material, so many fabricating processes were adopted to achieve sensing materials with nanoscale structure [1-3].

Electrospinning technique is commonly applied to prepare organic/inorganic nanocomposite fiber in the sub-microscale or nanoscale, due to its many attractive advantages, including suitable for various materials and the capability of generating the relatively large-scale continuous fibers [4,5]. In addition, electrospinning technique was used to prepare high-performance sensing chips due to its special characteristics, including low cost and simple process for the fabrication of high specific surface area.

In this study, we demonstrated a VOCs sensing chip consisting of P3HT/PMMA fiber and glass substrate, and it was fabricated by the electrospinning technique. The aligned P3HT/PMMA fibers shows the high sensitivity for toluene due to aligned P3HT/PMMA submicro fibers can influence the optical behavior definitely. The low cost, real-time, quick response, and high sensitivity P3HT/PMMA VOC sensor developed in the present work significantly widens the current VOC sensing technology and can be widely used to prevent the potential damages of VOCs.

2. Experimental Section

PMMA (MW~996,000Da, Aldrich) were used as received without further purification. The poly(3-hexylthiophene) (P3HT) was prepared by the related literature with some adjustments [6]. P3HT solution was obtained from P3HT dissolved in chlorobenzene (CB) with continuous stirring at 40ºC for 48 h. Then, P3HT solution was added to the stirred PMMA solution. During the electrospinning process, we fixed the constant flow rate at 1.0 ml/h; the distance between tip and collector was fixed at 7.0 cm and applied high-voltage 15.0 kV. The rotational speed was 80 rpm for the metallic collector. The excess VOC liquid was added into an enclosed 80 mL quartz container with the P3HT/PMMA sensing chip on the center of the container to sense VOC vapor at saturation vapor pressure. In addition, for sensing low concentration VOC vapor, controlled amounts of VOC liquid was added into the same container. After the liquid VOC evaporated in the bottle completely, we can obtain the controlled vapor concentration. The UV-Vis spectrometer (JASCO, V-630, Japan) was applied to investigate the absorption spectra of the P3HT/PMMA sensing chip. All the synthesis and sensing processes demonstrated above were completed in air.

In addition, the sensitivity, S, of the sensing chip were defined by observing the change of extinction spectra at different wavelength, such as 560 nm, 600 nm and 1020 nm. The equation of S of the sensing chip at 560, 600 and 1020 nm are shown as below:

$$S_{560} = \frac{\mathrm{I}_{560after} - \mathrm{I}_{560before}}{\mathrm{I}_{560before}} \qquad (1)$$

$$S_{600} = \frac{I_{600after} - I_{600before}}{I_{600before}} \qquad (2)$$

$$S_{1020} = \frac{I_{1020after} - I_{1020before}}{I_{1020before}} \qquad (3)$$

3. Results and Discussion

We prepared various P3HT/PMMA blend solutions with different P3HT concentration to fabricate P3HT/PMMA fibers by electrospinning process. After optimizing the following parameters of electrospinning process: **(a)** applied voltage, **(b)** tip-to-collector distance, **(c)** rotational speed of the metallic collector, and **(d)** nanocomposite solution flow rate, the P3HT/PMMA blend fibers on the glass substrate were obtained successfully. The surface microstructure of various P3HT/PMMA sensing chips, including (Type I) P3HT/PMMA film type, (Type II) random P3HT/PMMA fiber type and (Type III) aligned P3HT/PMMA fiber type are shown in **Figure 1 (a-c)**, respectively. The regular arrangement of aligned P3HT/PMMA submicro fibers on the sensing chip was observed, and the diameter of aligned P3HT/PMMA fibers on Type III sensing chip is about 1.40 μm that is similar to random fibers on Type II sensing chip as shown in **Figure 1 (c)**. **Figure 1(d-f)** shows the extinction spectra for various P3HT/PMMA sensing chips. Type III sensing chip consisted of aligned P3HT/PMMA submicro fibers exhibited the highest extinction behavior variation among these sensing chips. Especially, the intensity of extinction at 1,020 nm had significant change from 0.24 to 0.31. The corresponding sensitivity of Type III sensing chip exposed to saturated toluene for different time, including S_{560}, S_{600} and S_{1020}, is shown in **Figure 1(i)**. To begin with the sensing mechanism of Type III sensing chip, the surface of aligned P3HT/PMMA submicro fibers adsorbed the VOCs, when the sensing chip exposed to the VOCs. The VOCs vapor exhibited swelling behavior, so the sensitivity showed the increased trend. Then, the saturated VOCs vapor adhered to P3HT/PMMA fiber that led to the fiber collapse and form the flat and ribbon fibers, so the sensitivity showed the decreased trend. Furthermore, the flat and ribbon P3HT/PMMA fibers adsorbed a minor amount of VOCs vapor and showed the swelling behavior continuously, so the sensitivity showed the increase. Finally, the flat and ribbon P3HT/PMMA materials was removed slightly from the sensing chip substrate because of solvent annealed behavior. Type III sensing chip with aligned P3HT/PMMA submicro fibers exhibited the highest extinction variation among all sensing chips due to the aligned fiber chip was exposed to saturated toluene. The extinction spectra of Type III sensing chip showed large variation due to more fiber presented in the aligned structure and adsorb more solvent.

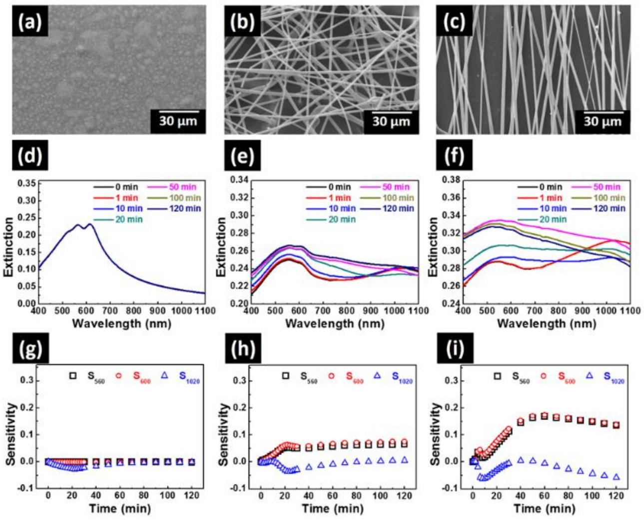

Fig. 1 (a-c) The microstructures of various sensing chips, including **(a)** Type I: P3HT/PMMA film, **(b)** Type II: random P3HT/PMMA fiber and **(c)** Type III: aligned P3HT/PMMA fiber, observed by SEM. **(d-f)** Extinction spectra of various sensing chips, including **(d)** Type I, **(e)** Type II, and **(f)** Type III. **(g-i)** The Sensitivities of various sensing chips, including **(g)** Type I, **(h)** Type II, and **(i)** Type III, exposed to saturated toluene for different time.

4. Conclusions

The various VOCs sensing chips fabricated from P3HT/PMMA were prepared successfully by the electrospinning technique in this study. The sensing chip consisted of aligned P3HT/PMMA fibers exhibited the obvious change of extinction spectra after exposure of VOCs. While the aligned fiber chip was exposed to saturated toluene, the extinction spectra showed large variation which is attributed to the more fibers presented in the aligned structure and thus it can adsorb more solvent.

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