SCIENCE CHINA
Technological Sciences

August 2013 Vol.56 No.8: 1877–1882
doi: 10.1007/s11431-013-5268-4

# The fabrication and optimization of OTFT formaldehyde sensors based on Poly(3-hexythiophene)/ZnO composite films

LI Xian, JIANG YaDong, TAI HuiLing*, XIE GuangZhong & DAN WenChao

*State Key Laboratory of Electronic Thin Films and Integrated Devices, School of Optoelectronic Information, University of Electronic Science and Technology of China (UESTC), Chengdu 610054, China*

Received March 18, 2013; accepted April 26, 2013

Formaldehyde (HCHO), a colorless and pungent-smelling gas, is confirmed be a huge threat to human health. The detection of formaldehyde is necessary and important. The Poly(3-hexythiophene) (P3HT)/ZnO organic-inorganic composite thin film was fabricated and used as the sensitive layer of organic thin film transistors (OTFT) by spray-deposited method to detect HCHO at room temperature. The process parameters such as P3HT/ZnO weight ratios and airbrushed masses were optimized. The results showed that P3HT/ZnO OTFT exhibited good sensing response to HCHO. Airbrushed mass of 1ml was the optimal mass, and the 1:1 and 1:5 weight ratios of P3HT/ZnO exhibited better sensing properties compared with others. OTFT gas sensors based on P3HT/ZnO composite film provides a novel promising approach to the detection of HCHO.

**formaldehyde, Poly (3-hexythiophene)/ZnO, composite, Organic Thin Film Transistors (OTFT)**

**Citation:** Li X, Jiang Y D, Tai H L, et al. The fabrication and optimization of OTFT formaldehyde sensors based on Poly(3-hexythiophene)/ZnO composite films. Sci China Tech Sci, 2013, 56: 1877–1882, doi: 10.1007/s11431-013-5268-4

## 1 Introduction

Formaldehyde (HCHO) is a colorless irritating odor at room temperature and has a characteristic pungent. Exposure to HCHO is a significant threat for human health. It is one of the contributors to the “sick building syndrome” typified by acute health effects such as irritative symptoms involving eyes and respiratory organs experiences by the occupants of a building. The allowed long-term exposure limit for HCHO is 1 ppm, while throat and nasal irritation can occur at levels of 0.08 ppm [1]. The US National Toxicology Program has described HCHO as “known to be a human carcinogen”.

Quartz crystal microbalance (QCM) [2], piezoelectric crystal [3] and cataluminescence [4] have been reported to apply in the fabrication of HCHO sensor. The methods of laser [5] and ultraviolet light irradiation [6] are also reported to detect HCHO. Metal oxides [7], such as ZnO, NiO, CdO, and $TiO_2$, are widely used for the sensitive materials of HCHO sensor. Nanomaterials [2, 8, 9] such as nanorods, nanofibrous, nanowires and carbon nanotubes, are applied for the HCHO sensor with the rising interest of nanotechnology. However, most HCHO sensors based on oxide thin films are reported to be operated at temperatures of 200°C–400°C.

Organic thin film transistor (OTFT) is a promising sensor device for an electronic olfaction platform with all the required features (sensitivity, reliability, and reproducibility) at low cost [10, 11]. Compared with other classical sensors, OTFT sensor can provide more information from changes in multiple properties on exposure to analyte, for example the transistor threshold voltage, field-effect mobility, the field-induced conductivity and the source-drain current [12]. Our previous research has shown that OTFT based on CuPc film has little response to 290 ppm HCHO vapor [13]. Poly(3-

*Corresponding author (email: taitai1980@uestc.edu.cn)

hexythiophene) (P3HT) is one of the widely used semiconductor materials in OTFT. The research about sensors based on P3HT sensitive film have been mainly reported on the detection of gases such as $NO_2$, $N_2O$, $NH_3$ and so on [14–16]. OTFT based on P3HT/ZnO nanomaterial has been reported to enhance charge mobility of the device [17]. But HCHO sensor based on P3HT/ZnO OTFT has never been reported.

In this paper, sprayed P3HT/ZnO composite sensitive films are fabricated as the sensitive layer of OTFT sensors to detect HCHO at room temperature. The electrical characteristics and HCHO -sensing properties of P3HT/ZnO-OTFT sensor with different airbrushed mass and different weight ratios were studied.

## 2 Experimental

The typical OTFT was given in Figure 1. In this scheme, transistors were made in a bottom contact configuration on a Sb-doped n+-type (0.02 Ω cm) Czochralski (CZ)-grown silicon wafer, which was also used as an ohmic contact functions as the gate electrode. The gate dielectric layer was thermal $SiO_2$ with 195 nm in thickness. Gold source and drain electrodes (a 20 nm-thick Ti layer was used under a 50 nm-thick Au layer for adhesion between the Au layer and insulator layer) were deposited on the top of the gate dielectric through a shadow mask with a defined channel width and channel length of 4000 and 25 μm, respectively [18].

Spray-deposited [19–21] organic thin-film transistors with P3HT/ZnO composite active layer were fabricated using an airbrush (HOLDER180, Taiwan HD corp.) with pressurized nitrogen as the carrier gas. The distance between the bottom of OTFT and the top of airbrush was 8 cm and the flow rate was about 10 μL/s. P3HT(purchased from Luminescence Technology Corp.) was dissolved in chloroform (3 mg/mL). ZnO nanoparticle dispersion (purchased from Sigma-Aldrich, 40 wt% in ethanol, <130 nm) was diluted in ethanol (3 mg/mL), and then added into P3HT solutions. The mixed solution was slightly agitated using a glass bar and then ultrasonicated (KQ-250 digital controlled ultrasonic machine, KunShan Province ultrasonic instrument factory) for 10 min. To study the effect of airbrushed mass on sensing properties, 1:1 weight ratio of P3HT/ZnO with different airbrushed mass were fabricated. The airbrushed masses were from 0.6 to 1.4 mL with a step of 0.2 mL, and the samples with different P3HT: ZnO weight ratios of 1: 0.2, 1:0.33, 1:1, 1:3 and 1:5 were also prepared.

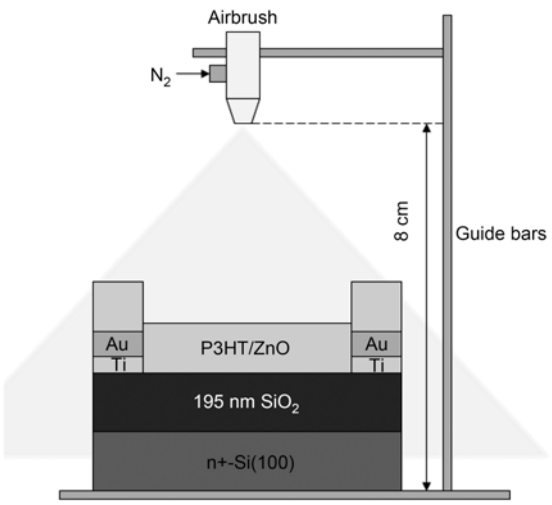


**Figure 1** Schematic drawing of the spray deposition setup and structure of OTFT.

The thin film morphology was studied using a scanning electron microscope (SEM, Inspect). The current-voltage characteristics of the prepared OTFT were studied using a Keithley 4200-SCS source measurement unit. The gas concentrations were controlled using a mass flow controls (MT50-4J, Beijing Metron Instruments Co. Ltd., China). The HCHO gas (506 ppm, $N_2$ as the balance gas) was supplied by Beijing Beiyang Special Institute Co., Ltd. The dry air was used as the carrier gas (Chengdu Dongfeng Gas Factory).

In this measurement, OTFT devices were operated in the accumulation mode by applying negative gate bias, while the source electrode was grounded and the drain electrode was negatively biased. All the measurement results were obtained at room temperature in the dry air atmosphere.

## 3 Results and discussion

### 3.1 Influence of airbrushed mass on sensing properties of P3HT/ZnO OTFT sensors

The bottom contact P3HT/ZnO OTFT was operated in the accumulation mode (gate negatively biased). Take P3HT/ZnO OTFT with 1:1 weight ratio and 1mL airbrushed mass for example (Figure 2). The drain voltage ($V_{ds}$) sweeps from 0 to −60 V at gate bias ($V_{gs}$) between 0 to −50 V in a step of −10 V. The drain-source current ($I_{ds}$) in the linear and saturation regions of OTFT is given by eqs. (1) and (2), respectively [21].

$$I_{ds} = \frac{WC_i\mu}{L}\left[(V_{gs}-V_{th})V_{ds}-\frac{1}{2}V_{ds}^2\right], \quad (1)$$

$$I_{dsat} = \frac{WC_i\mu}{2L}(V_{gs}-V_{th})^2, \quad (2)$$

where $W$ and $L$ are the channel width and length, $C_i$ is the capacitance of the insulator, $\mu$ is the carrier mobility, $V_{ds}$ is drain voltage, and $V_{th}$ is threshold voltage. $C_i$ is given by eq. (3)

$$C_i = \frac{\varepsilon_i\varepsilon_0}{d}, \quad (3)$$

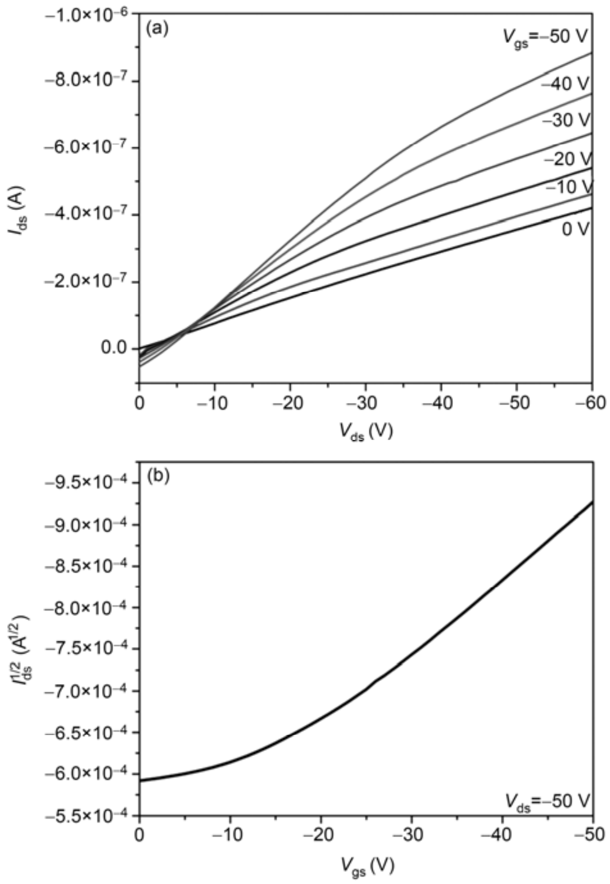


**Figure 2** Electrical characteristics of sprayed P3HT/ZnO (1:1 ratio by weight)-OTFT with 1ml airbrushed mass. (a) $I_{ds}$-$V_{ds}$ characteristics at different gate biases; (b) transfer characteristics at $V_{ds}$=−50 V.

where $d$ is the thickness of insulator layer and is 195 nm; $\varepsilon_i$ is dielectric constant of $SiO_2$ insulator layer and equals to 3.9. $\varepsilon_0$ is the vacuum capacitance and equals to $8.85\times10^{-14}$ F/cm. The calculated $C_i$ is 17.7 nF/cm$^2$. Mobility values in the saturation regime can be calculated using eq. (2). $V_{th}$ is the intersection of the linear curves with the $X$ axis.

The thickness of spray-deposited films could not been accurately determined with measurement instrument due to rough and soft surfaces [20]. So the airbrushed mass was used to define the approximate thickness of the sensitive films. Five different airbrushed masses of 0.6, 0.8, 1, 1.2 and 1.4 mL were adopted to fabricate sensitive films.

The sensing properties of five devices to 100 ppm HCHO were investigated. In this experiment, the drain-source on-current ($I_{ds}$) in a working point ($V_{ds}$=−50 V, $V_{gs}$=−30 V) was firstly considered as the key parameter to evaluate the gas sensing properties. Figure 3 showed the real-time response of P3HT/ZnO (1:1) OTFT with different airbrushed masses to 100 ppm HCHO at room temperature. HCHO was added in the measurement body after the device stabilized under dry air atmosphere. The $I_{ds}$ decreases dramatically once the HCHO was introduced, and then returned to its initial value slowly when the HCHO source was turned off.

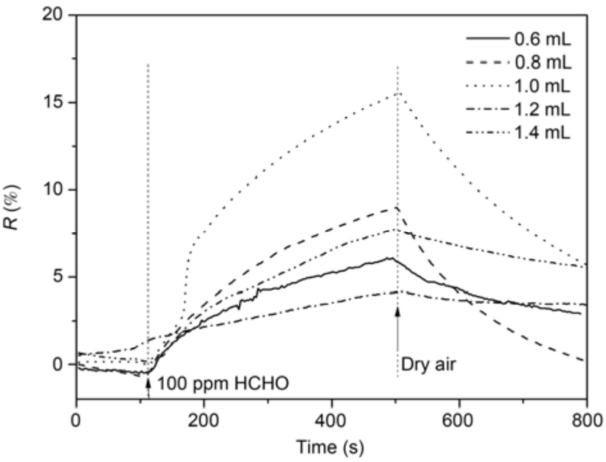


**Figure 3** Sensing response curve of P3HT/ZnO OTFT (1:1 ratio by weight) with different airbrushed mass to 100 ppm HCHO at room temperature (response time 400 s).

The sensing response of the film was defined by $R$ (%)= $100(I_{air}-I_{gas})/I_{air}$, where the $I_{gas}$ and $I_{air}$ were $I_{ds}$ with and without the existence of HCHO gas. A positive value of $R$ implies that the OTFT current decreases to HCHO and vice versa.

As shown in Figure 3, the sensing property had strong dependence on the thickness of thickness film, and the device with 1 mL airbrushed mass exhibited the greatest sensing response among five devices. The changes of threshold voltage and mobility were summarized in Table 1. The device with 1 mL airbrushed mass possessed the optimal properties to 100 ppm HCHO for the maximal changes of threshold voltage and mobility compared with other devices, which was also coincident with the sensing response. Change of threshold voltage ($\Delta V_{th}$) was defined by $\Delta V_{th}$= $(V_{th})_{air}-(V_{th})_{gas}$, and change of mobility ($\Delta u$) was defined by $\Delta u=u_{air}-u_{gas}$. These results also proved that OTFT was multi-parameter sensor.

Effective OTTF sensors required that the $I_{ds}$ must change enough to distinguish from the noise and the base line drift. At the same time, the responses of sensors must be fast enough for the application. Therefore, the sensitive active layer was as thin as possible, so that analyte would influence the sensitive layer strongly and rapidly [22]. Organic active layer is required to fabricate on the top of the 70 nm Ti/Au electrode layer in this paper. The thickness of sensi-

**Table 1** Parameter changes of sprayed P3HT/ZnO (1:1 ratio by weight) OTFT with different airbrushed mass to 100 ppm HCHO at room temperature (response time 400 s)

| Airbrushed mass (mL) | $\Delta V_{th}$ (V) | $\Delta u$ (cm$^2$/Vs) | Response (%) |
|---|---|---|---|
| 0.6 | 7 | $0.83\times10^{-5}$ | 6.09 |
| 0.8 | 10 | $0.09\times10^{-5}$ | 8.99 |
| 1.0 | 23 | $1.21\times10^{-5}$ | 15.69 |
| 1.2 | 4 | $0.06\times10^{-5}$ | 4.14 |
| 1.4 | 9 | $0.02\times10^{-5}$ | 7.71 |

tive layer must be greater than 70 nm. So, too thin or too thick film was not helpful to the response and recovery of gas sensor. Based on the above results, 1ml airbrushed mass was chosen for the following research.

### 3.2 Effect of P3HT: ZnO ratio in composite films on sensing properties

Besides the devices with different airbrushed mass, the devices with different P3HT: ZnO weight ratio in composite films were also fabricated. Figure 4 showed the real-time sensing response curve of sprayed P3HT/ZnO OTFT sensor with different weight ratios exposed to 100 ppm HCHO at room temperature. $I_{ds}$ changed immediately when P3HT/ZnO OTFTs were exposed to HCHO. The adsorption of HCHO on the sensitive film surface donated electron, thereby increasing its resistance and accordingly $I_{ds}$ decreased [23, 24]. As the amount of HCHO molecules adsorbed on the P3HT/ZnO attained saturate, $I_{ds}$ became changeless and tended to stable. It could be seen that the P3HT/ZnO OTFTs with weight ratios of 1:3 and 1:5 exhibited an opposite response to 100 ppm HCHO comparing with other three OTFT sensors, $I_{ds}$ increased when exposed to HCHO. The sensing response and changes of threshold voltage and mobility before and during the exposure to HCHO exhibited conformably and all were negative, as shown in Table 2. These results validated that added n-type ZnO plays an important role in composite films. With the increasing ratio of n-type ZnO nanoparticle, the major role of p-type P3HT may be reduced by donating electron [25].

Figure 5 represented SEM images of spray-deposited P3HT/ZnO composite films with different weight ratios. It can be seen that the P3HT/ZnO composite films were fairly uniform and discontinuous at the micro-scale and ZnO nanoparticle was uniformly dispersed in P3HT. The films exhibited large surface area and many adsorption sites, which were desired for the gas sensor application. So the film with 1:1 weight ratio was manifested better response than that

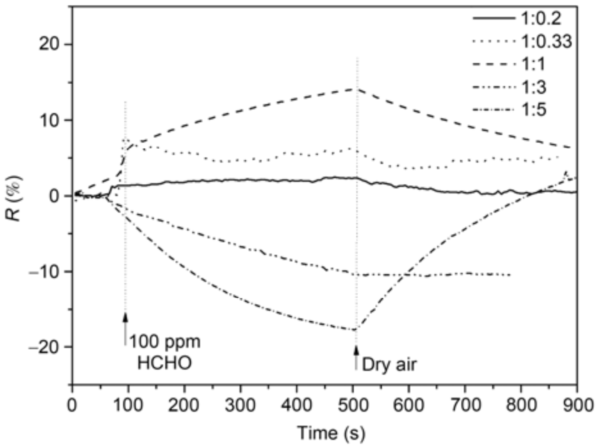


**Figure 4** Sensing response curve of P3HT/ZnO OTFTs with different weight ratios to 100 ppm HCHO at room temperature (response time 400 s).

**Table 2** Parameter changes of P3HT/ZnO OTFT with different weight ratios to 100 ppm HCHO at room temperature

| Composition (P3HT:ZnO) | $\Delta V_{th}$ (V) | $\Delta u$ ($cm^2$/V s) | Response (%) |
|---|---|---|---|
| 1:0.2 | 2 | $1.8\times10^{-5}$ | 2.53 |
| 1:0.33 | 10 | $7.8\times10^{-5}$ | 6.10 |
| 1:1 | 23 | $1.21\times10^{-5}$ | 15.69 |
| 1:3 | −2 | $-3.63\times10^{-5}$ | −10.60 |
| 1:5 | −5 | $-6.36\times10^{-5}$ | −18.3 |

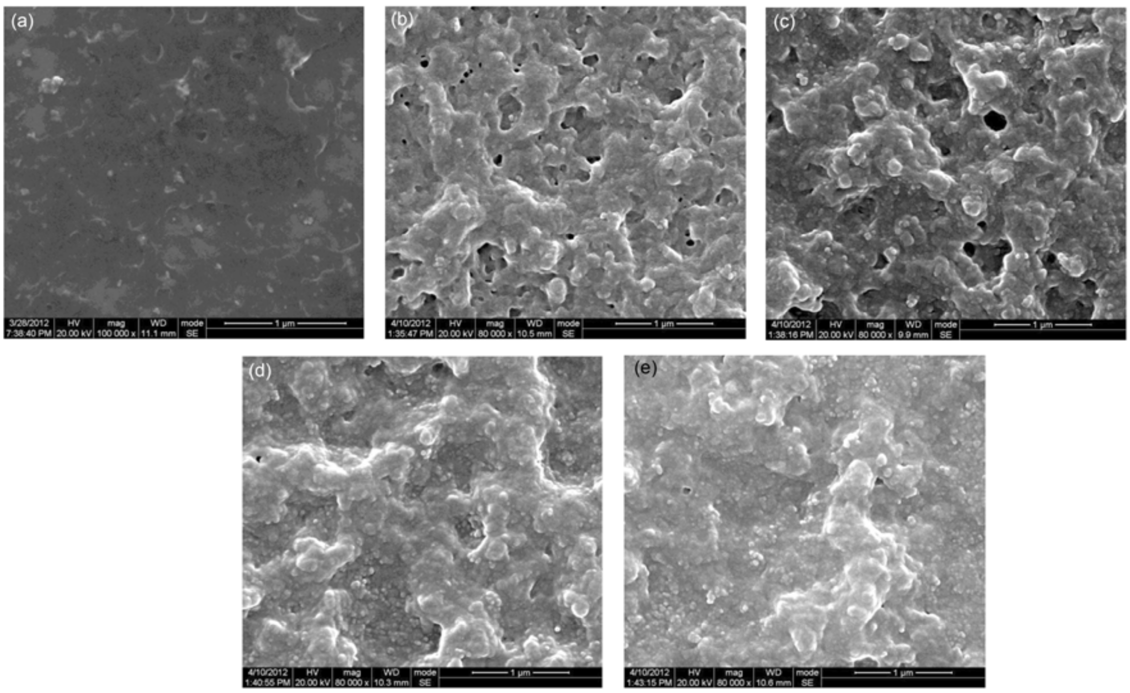

**Figure 5** SEM graphs of sprayed P3HT/ZnO composite films with weight ratio of (a) 1:0.2, (b) 1:0.33, (c) 1:1, (d) 1:3 and (e) 1:5.

with 1:0.2 and 1:0.33. The film with 1:3 and 1:5 showed that ZnO nanoparticles were existed the whole surface of the film, and ZnO played more important roles in the process of HCHO-sensing response compared with P3HT.

The incorporating ZnO nanoparticles can modulate the energy between the work function of the Au electrode and the ionization potential of P3HT, reducing the contact resistance and enhancing the charge injection of hole carriers. In general, the energy level of ZnO was in the range from –4.2 to −7.6 eV [25]. Figure 6 showed an idealized depiction of the energy level in the composite films at the contact vicinity. The introduction of ZnO nanoparticles may partially serve to improve the injection barrier at the Au/ P3HT contact interface. At the same time, the introduction of ZnO nanoparticles served to response to HCHO as well [26, 27].

The P3HT/ZnO OTFT exhibited different response to other 100 ppm reductive gases such as CO, $H_2S$, $NH_3$, $H_2$ and $CH_4$, as shown in Figure 7. The reason might be ascribed to the polarity and the abilities of donating electron of gases [28]. The oxygen in C=O bond of HCHO molecule had the strong binding ability with conjugated π bond of P3HT and P3HT/ZnO OTFTs exhibited the largest response.

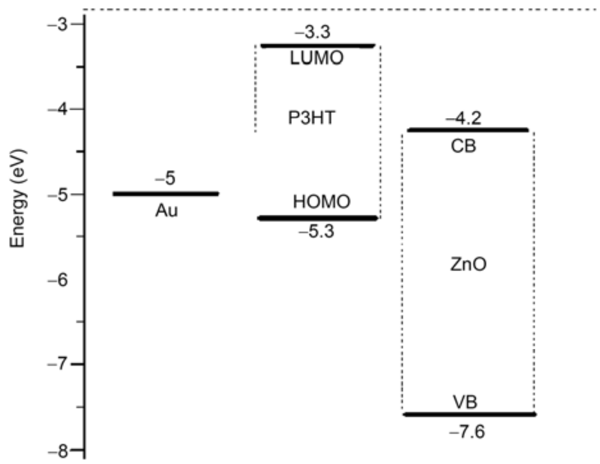


**Figure 6** Schematic idealized energy band diagram.

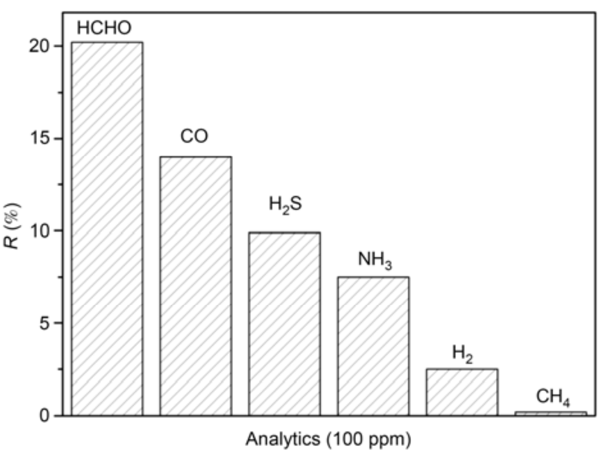


**Figure 7** Selectivity of P3HT/ZnO OTFT.

## 4 Conclusions

Bottom-contact OTFTs with sprayed P3HT/ZnO composite films as active layer were fabricated in this paper. The sprayed P3HT/ZnO OTFT exhibited good sensing response to HCHO and good selectivity at room temperature. The OTFT with 1 ml airbrushed mass showed best sensing response compared with other airbrushed mass, which manifested that the sensing properties has dependence on the thickness of sensitive film. The proportion of ZnO nanoparticle in composite films extremely influenced the electric characteristics and sensing properties of P3HT/ZnO OTFTs. The experiment results represented that added ZnO nanoparticle played an important role in the sensing response to HCHO. The sensitive materials and sensing properties of OTFT HCHO sensor would be deeply researched in future.

*This work was supported by the National Natural Science Foundation of China (Grant Nos. 61176066, 61101031).*

1 Ryan M A, Zhou H, Buehler M G, et al. Monitoring space shuttle air quality using the Jet Propulsion labotatory electronic nose. IEEE Sensor J, 2004, 4: 337–347
2 Hu W L, Chen S Y, Liu L T, et al. Formaldehyde sensors based in nanofibrous polyethyleneimine /bacterial cellulose membranes coated quartz crystal microbalance. Sens Actuators B, 2011, 157: 554–559
3 Filho O F, Suleiman A A, Guilbault G G. Piezoelectric crystal sensor for the determination of formaldehyde in air. Talanta, 1991, 38: 541–545
4 Zhou K W, Ji X L, Zhang N, et al. On-line monitoring of formaldehyde in air by cataluminescence-based gas sensor. Sens Actuators B, 2006, 119: 392–397
5 Horstjann M, Bakhirkin Y A, Kosterev A A, et al. Formaldehyde sensor using interband cascade laser based quartz-enhanced photoacoustic spectroscopy. Appl Phys B, 2004, 79: 799–803
6 Peng L, Zhao Q D, WangD J, et al. Ultraviolet-assisted gas sensing: A potential formaldehyde detection approach at room temperature based on zinc oxide nanorods. Sens Actuators B, 2009, 136: 80–85
7 Han N, Tian Y J, Wu X F, et al. Improving humidity selsectivity in formaldehyde gas sensing by a two-sensor array made of Ga-doped ZnO. Sens Actuators B, 2009, 138: 228–235
8 Wang R X, Zhang D J, Zhang Y M, et al. Boron-doped carbon nanotubes serving as a novel chemical sensor for formaldehyde. J Phys Chen B, 2006, 110: 18267–18271
9 Lu Y J, Meyyappan M, Li J. A carbon-nanotube-based sensor array for formaldehyde detection. Nanotechnol, 2011, 11: 055502
10 Wang L, Fine D, Sharma D, et al. Nanoscale organic and polymeric field-effect transistors as chemical sensors. Anal Bioanal Chem, 2005, 384: 310–321
11 Street R A, Thin-film transistors. Adv Mater, 2009, 21: 2007–2022
12 Torsi L, Dodabalapur A, Sabbatini L, et al. Multi-parameter gas sensors based on organic thin-film-transistors. Sens Actuators B, 2007, 67: 312–316
13 Yan J F, Wu Z M, Tai H L, et al. The investigation of the formaldehyde gas sensor based on organic thin-film transistors. In: The IEEE International Conference on Apperceiving Computing and Intelligence Analysis. Chengdu: IEEE, 2010. 213–216
14 Liu B, Xie G Z, Du X S, et al. Poly (3-hexylthiophene) based organic

field-effect transistor as $NO_2$ gas sensor. Proc SPIE, 2009, 7508: 750813-1
15 Fukuda H, Yamagishi Y, Ise M, et al. Gas sensing of properties of Poly-3-hexylthiophene thin film transistors. Sens Actuators B, 2005, 108: 414–417
16 Jeong J W, Lee Y D, Kim Y M, et al. The response characteristics of a gas sensor based on Poly-3-hexylthiophene thin-film transistors. Sens Actuators B, 2010, 146: 40–45
17 Navan R R, Panigraphy B, Baghini M S, et al. Mobility enhancement of solution-processed Poly (3-hexylthiophene) based organic transistor using zinc oxide nanosturctures. Compos Part B-Eng, 2012, 43: 1645–1648
18 Li X, Jiang Y D, Xie G Z, et al. Copper phthalocyanine thin film transistors for hydrogen sulfide detection. Sens Actuators B, 2013, 176: 1191–1196
19 Green R, Morfa A, Ferhuson A J, et al. Performance of bulk heterojunction photovoltaic devices prepared by airbrush spray deposition. Appl Phys Lett, 2008, 92: 033301
20 Chan C K, Richter L J, Dinardo B, et al. High performance airbrushed organic thin film transistors. Appl Phys Lett, 2010, 96: 133304
21 Azarova N A, Owen J W, Mclellan C A, et al. Fabrication of organic thin-film transistors by spray-deposition for low-coat, large-area electronics. Org Electron, 2010, 11: 1960–1965
22 Someya T, Dodabalapur A, Huang J, et al. Chemical and physical sensing by organic field - effect transistors and related devices. Adv Mater, 2010, 22: 3799
23 Guillaud G, Simon J, Germain J P. Metallophthalocyanines Gas sensors, resistors and field effect transistors. Chem Soc Rev, 1998, 178–180: 1433–1484
24 Bohrer F I, Sharoni A. Gas sensing mechanism in chemiresistive cobalt and metal-free phthalocyanine thin films. J Am Chem Soc, 2007, 129: 5640–5646
25 Saxena V, Aswal K D, Kaur M, et al. Enhanced $NO_2$ selectivity of hybrid poly(3-hexylthiophene): ZnO-nanowire thin films. Appl Phys Lett, 2007, 90: 043516
26 Hsieh G W, Li F M, Beecher P, et al. High performance nanocomposite thin film transistors with bilayer carbon nanotube-polythiphene active channel by ink-jet printing. J Appl Phys, 2009, 106: 123706
27 Park Y D, Lim J A, Jiang Y, et al. Enhancement of the field-effect mobility of poly(3-hexylthiophene)/functionalized carbon nanotube hybrid transistors. Org Elec, 2008, 9: 317–322
28 Trogler W C. Chemical sensing with semiconducting metal phthalocyanines. Struct Bond, 2012, 142: 91–118