

Conjugated Polymer/Nanoparticles Nanocomposites for High Efficient and Real-Time Volatile Organic Compounds Sensors

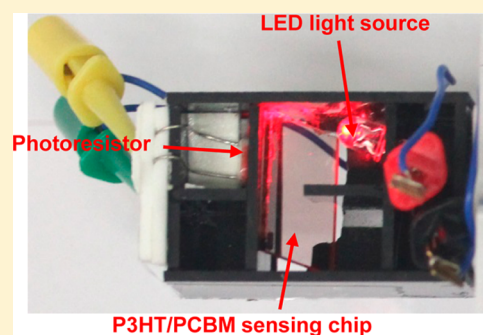
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W Web-Enhanced Feature **S** Supporting Information

ABSTRACT: The present work demonstrates a high efficient and low cost volatile organic compounds (VOCs) sensor. Nowadays, VOCs, which are typically toxic, explosive, flammable, and an environmental hazard, are extensively used in R&D laboratories and industrial productions. Real-time and accurately monitoring the presence of harmful VOC during the usage, storage, or transport of VOCs is extremely important which protects humans and the environment from exposure in case of an accident and leakage of VOCs. The present work utilizes conducting polymer/nanoparticles blends to sense various VOCs by detecting the variation of optical properties. The novel sensor features high sensitivity, high accuracy, quick response, and very low cost. Furthermore, it is easy to fabricate into a sensing chip and can be equipped anywhere such as a laboratory or a factory where the VOCs are either used or produced and on each joint between transporting pipes or each switch of VOC storage tanks. Real-time sensing is achievable on the basis of the instant response to VOC concentrations of explosive limits. Therefore, an alarm can be delivered within a few minutes for in time remedies. This research starts from investigating fundamental properties, processing adjustments, and a performance test and finally extends to real device fabrication that practically performs the sensing capability. The demonstrated results significantly advance the current sensor technology and are promising in commercial validity in the near future for human and environmental safety concerns against hazardous VOCs.



In various R&D laboratories, industrial productions, such as semiconductor, petroleum, chemical, etc., and volatile organic compounds (VOCs) are extensively used during experiments and productions. They sometimes act as reagents or raw materials for making new chemicals and materials. Other applications such as developing agents and cleaning liquids for printed wiring boards, fuels for transportation vehicles, etc. also include VOCs. VOCs are typically dangerous, explosive, flammable, toxic, and environmentally hazardous. Usage, leakage, or spillage of the compounds would generate organic vapors. When they are in an excess amount over the limits explosion, environmental pollution, fire accidents, explosions, etc. result and thus serious injuries, deaths, and extensive property loss occur. For example, the refinery explosion in Texas City, U.S.A. due to an oil spillage caused over 100 people to be injured and 15 were confirmed dead.¹ Furthermore, exposure of the human body to VOCs accounts for higher rates of diseases such as allergy, cancer, asthma, etc. Therefore, the storage, transport, and usage of VOCs should be extremely careful. The real-time detection of the toxic compounds is hence important which ensures the safety of human health and properties and also avoids environmental disasters. The study of sensing VOCs starts from 1982 when Dodd and Persaud et al. demonstrated the concept of electronic nose.^{2,3} It is an electronic device analogous to the human nose which can distinguish the flavor fingerprints among different compounds

by detecting the signal variations such as resistance, voltage, current, frequency, etc. Recently, numerous methodologies have been demonstrated to sensing VOCs such as semiconductor sensing,^{4–6} catalytic combustion,^{7,8} electrochemistry sensing,^{9–11} infrared sensing,^{12–15} etc. These methodologies have been applied to commercialized sensor products nowadays. However, most of the above-mentioned sensors are extremely expensive. For example, an infrared sensor for sensing the VOCs leakage costs over 130,000 U.S. dollars which apparently limits the popularity and extensive usage. Specifically, to our best knowledge, there is no commercial VOC sensor to date that can be massively installed and equipped everywhere such as the laboratory and factory where the VOCs are either used or produced. Particularly, the joint between transporting pipes or each switch of VOC storage tanks are all with high risk of VOC leakage. Therefore, the purpose of the present research is to develop a low-cost, high sensitivity, and high accuracy VOC sensor that can be equipped in which the VOCs are being used/produced with real-time detection. The functionality of the sensors is expected to promptly and accurately alarm the exceeding concentration of VOCs which enables remedies in time.

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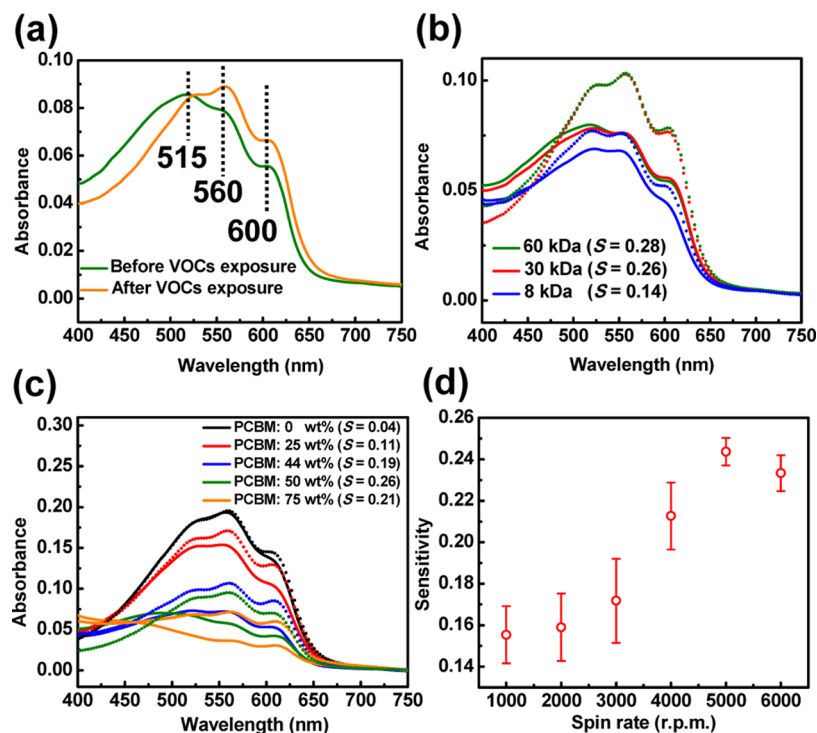


Figure 1. (a) Absorption spectra of P3HT/PCBM film before and after chlorobenzene vapor exposure for 2 h. The dot lines indicate the characteristic absorption peaks centered at 515, 560, and 600 nm, respectively. (b) Absorption spectra of P3HT/PCBM with different M_w of P3HT, i.e., 8, 30, and 60 kDa before (solid lines) and after (dotted lines) chlorobenzene vapor exposure, respectively. (c) Absorption spectra of P3HT/PCBM with different blending ratios, i.e., 0, 25, 50, and 75 wt % of PCBM before (solid lines) and after (dotted lines) chlorobenzene exposure, respectively. (d) The sensitivity of P3HT/PCBM (50 wt % PCBM) films deposited from different spin rates. The “S value” in the parentheses represents the sensitivity of each film.

Blends of conducting polymer and nanoparticles have been extensively investigated for optoelectronic device applications particularly the bulk heterojunction solar cells in which the two materials are intimately mixed. The poly(3-hexylthiophene) (P3HT)/[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) blend is the most famous system over the past decade.^{16,17} The three-dimensional (3D) nanomorphology of the P3HT/PCBM blending film is of interest because it can be manipulated by different post-treatments such as thermal annealing and solvent vapor annealing.^{16–21} In other words, it is believed that the 3D nanostructure of a blend thin film deposited from the fast drying process of spin coating is relatively unstable due to the limited time for molecular ordering. Therefore, the exposure of organic solvent vapors can lead to the rearrangement of nanomorphology. Specifically, the increased mobility of both P3HT and PCBM molecules immersed in solvent vapors results in higher order and phase-separated domains of each phase. The varied 3-D nanostructures and increased crystallinity consequently affect the behaviors of conjugated π electrons and thus the optical properties. The present study proposes a methodology of detecting the variation of optical property when a polymer/nanoparticle film is exposed to the VOC's vapor as a powerful indication of VOCs existing. This methodology can be widely applicable in different conducting polymer/nanoparticle blend or hybrid materials. The P3HT/PCBM is used as a representative example in the present study, and the sensing effect is moreover quantified with different VOCs in different concentrations and exposure time. The results demonstrate the significant sensing capability of conducting polymer/nanoparticles blend to VOCs, i.e., high sensitivity, high accuracy, real time detection, etc. and a

comprehensively established database. Finally, a real device adopting the proposed methodology was fabricated for exhibiting the practical VOCs sensing by transferring the optical signal variations to electronic signals. The demonstrated low cost and high efficient VOCs sensor significantly advance the current technology of protecting humans and the environment from risky damage of VOCs.

EXPERIMENTAL SECTION

All VOCs were purchased from ACROS with purity >99%. The P3HT with different molecular weights, i.e., 8, 30, and 60 kDa was synthesized according to our previous work.²² The PCPDTBT was purchased from 1-material Inc. PC₆₁BM and PC₇₁BM were purchased from Solenne B.V. Inc. with purity >99%. The detailed synthesis of TiO₂ nanorods and Cu₂S nanoparticles were reported elsewhere,^{23,24} and the transmission electron transmission (TEM) observations are shown in the Supporting Information, Figure S1.

The P3HT/PCBM solutions were prepared in chlorobenzene with 9 mg/mL concentration in different blending ratios and stirred at 40 °C for 2 days. Other blend or hybrid solutions, i.e., P3HT/PC₇₁BM, P3HT/Cu₂S, and P3HT/TiO₂, were also prepared in chlorobenzene of 9 mg/mL concentration and 1:1 weight ratio. Glass substrates were rinsed by ethanol, and the prepared solutions were deposited on the substrates by spin coating to obtain the as-cast films. To sense VOC vapor at saturation vapor pressure, excess VOC liquid was added into a 50 mL enclosed bottle with the as-cast film stuck inversely on the top of the bottle. On the other hand, for sensing VOC vapor with low concentration, controlled amounts of VOC liquid was added into a 1 L enclosed bottle, and thus,

controlled vapor concentration was obtained after the liquid VOC completely evaporated within the bottle. The ultraviolet–visible spectrometer (PerkinElmer Lambda 35) was utilized to measure the absorption spectrum of the blend films. All the fabrication and sensing procedures mentioned above were performed in air.

We employed a setup to practically perform the real-time VOC sensing procedure. This setup includes a sensor box which is composed of a sensing chip with P3HT/PCBM spin coated on glass substrate, a commercially available light emitting diode (LED) with wavelength of 650 nm as the light source, and a photoresistor for detecting the light intensity variation transmitting through the P3HT/PCBM sensing chip. The photoresistor was installed in a circuit and hence can transfer the light intensity variation to resistance variation. The circuit additionally includes a capacitor, a resistor, a warning light, a variable resistor, two transistors, a switch, a power supply, and a warning light. The scheme and picture of the circuit are shown in the Supporting Information, Figure S2. The resistance difference resulted from using an as-casted P3HT/PCBM film, and a VOC vapor exposed P3HT/PCBM film is found to be around 50–100 k Ω . Therefore, the variable resistors were used to tune the circuit and to turn on the warning light (flash) when the resistance variation of the photoresistor was larger than 50 k Ω . The sensing box was placed in a 6 L box which was used to create the environment with controlled concentration of VOC vapors. The cost of components used to set up the sensing system is lower than 4 U.S. dollars (including the sensing chip, the circuit, and the LED light).

RESULTS AND DISCUSSION

We first adopted P3HT/PCBM blend as a representative conducting polymer/nanoparticle blend for the following study. We started with taking chlorobenzene as a VOC example which is a very toxic compound and often used as a solvent. The absorption spectra of the as-cast P3HT/PCBM film and the films exposed to chlorobenzene vapor for 2 h under saturation vapor pressure are shown in Figure 1a. The 2 h exposure time used here is to make sure a saturated vapor of simulated VOC environment can be repeatedly achieved for the reproducibility of the study. For the actual sensing device, of course, one would need the response time to be as short as possible which will be discussed later. It can be observed that the absorbance reveals three characteristic peaks centered at 515, 560, and 600 nm. The latter two shoulders can be attributed to the π – π stacking of P3HT chains and are both closely correlated to the crystallinity.¹⁸ In contrast, the characteristic peak at 515 nm represents the intrachain conjugated π electrons which is mainly determined by the film thickness. The obviously increased intensities of 560 and 600 nm peaks after chlorobenzene vapor exposure thus suggest the improvement of P3HT crystallinity. We show a schematic representation of morphological variation of P3HT/PCBM blend film in the Supporting Information, Figure S3. The molecular ordering of P3HT in crystallites is also illustrated with indication of π – π stacking (Supporting Information, Figure S3). The ordering of amorphous P3HT chains into organized crystallites accounts for the remarkably enhanced π – π stacking and thus increased absorbance at wavelength of 560 and 600 nm. Hence, the significant variations of absorbance at 560 and 600 nm can be served as an indication of the existence of VOCs. The sensitivity can be thus quantified by either focusing on the

absorption variation at 600 or at 560 nm. Herein, we define the sensitivity S of the film according to the absorption variation at 600 nm as:

$$S = \frac{(A_{600}/A_{515})_a}{(A_{600}/A_{515})_b} - 1$$

where $(A_{600}/A_{515})_b$ and $(A_{600}/A_{515})_a$ are the absorbance ratio between 600 and 515 nm before and after VOC vapor exposure, respectively. We define the sensing error σ as the standard deviation of sensitivity obtained from more than 10 pieces of independently prepared and tested P3HT/PCBM films. Note that the absorbance at 515 nm (A_{515}) is served as the reference because it can exclude the effect of film thickness variation before and after VOCs exposure.

For maximizing the sensitivity and minimizing the sensing errors, we tuned different parameters based on the fundamental properties of materials and the film forming process. The main direction is apparent according to the proposed sensing principal. That is, high sensitivity can be achieved by either suppressing the crystallization of P3HT in the as-cast film or enhancing the P3HT crystallinity in VOC vapor exposed film. Note that the adjustments of the sensitivity and sensing errors with respect to materials and processing conditions in the following were also based on the exposure of chlorobenzene vapor under saturation vapor pressure for 2 h. It has been reported that a higher molecular weight (M_w) of P3HT tends to fold into a lamellar structure in which closer π – π stacking and more pronounced characteristic peaks in the absorption spectrum were observed.²⁵ Therefore, as shown in Figure 1b, the P3HT/PCBM with 60 kDa P3HT exhibits the highest sensitivity of 0.28 as compared with that of 8 kDa ($S = 0.14$) and 30 kDa ($S = 0.26$). Additionally, Figure 1c summarizes the sensitivities of the thin films spin-coated from different spin rates and their corresponding film thickness (Supporting Information, Figure S4 and Table S1). The results reveal that increasing the spin rate leads to the increased sensitivities and sensing accuracy. The spin rate of 5000 r.p.m. shows sensitivity S and sensing error σ of 0.24 and 6.5×10^{-3} , respectively, of which the variation error is considerably smaller than the detected sensitivity ($\sim 2.8\%$). It can be reasonably explained that higher spin rate forces the film to dry faster which leads to lower crystallinity of P3HT and more unstable morphology. A more significant absorbance difference can be thus obtained after VOC vapor exposure. It is noteworthy that the spin rate higher than 5000 r.p.m. results in slightly decreased sensitivity. This can be attributed to the thinner film that would in contrast limit the reordering of polymer chains into crystallite due to the substantial crystal size of ~ 20 nm.¹⁹ Therefore, the spin rate was optimized to be 5000 r.p.m. with the film thickness of ~ 58 nm (Supporting Information, Table S1) which provides the highest sensitivity and also the highest sensing accuracy. Besides, the blending ratio of P3HT/PCBM was also tuned as shown in Figure 1c of the absorption spectrum and calculated sensitivities. Apparently, the optimized blending ratio is shown to be 50 wt % PCBM which can be explained: a substantial loading amount of PCBM is required which interrupts the packing of polymer chains and thus inhibits the crystallization in the as-cast film. However, a too high loading amount of 75 wt % would in turn hinder the P3HT chain folding into ordered structure during VOC vapor exposure. As a result, the highest sensitivity of 0.26 is obtained when blending the P3HT and PCBM in an equal amount of weight.

We tried to verify that the proposed concept is applicable in other blend or hybrid materials and clarify the mechanism of sensing, i.e., sensing VOCs by the difference of optical property that resulted from morphological variation of conducting polymer/nanoparticles blends or hybrids. We used other kinds of nanoparticles or nanorods (Supporting Information, Figure S1), i.e., PC₇₁BM, TiO₂ nanorods (25 nm in length and 5 nm in width), and Cu₂S nanoparticles (5–6 nm in diameter) in blends with P3HT, respectively. The obtained sensitivity *S* is shown in Table 1, together with pristine P3HT for comparison.

Table 1. Sensitivity of Pristine P3HT and Different Conducting Polymer/Nanoparticles Blends or Hybrid Films with Blending Weight Ratio of 1:1^a

thin film	nanoparticle size (nm)	sensitivity
pristine P3HT	n/a	0.04
P3HT/TiO ₂	20 ^b	0.00
P3HT/Cu ₂ S	5	0.07
P3HT/PC ₆₁ BM	0.7	0.26
P3HT/PC ₇₁ BM	0.7	0.67

^aThe sensitivities were obtained from exposing the films to chlorobenzene vapor for 2 h at saturation vapor pressure. ^bThe TiO₂ is a nanorod with an average size of 20 nm in length and 5 nm in width (cf. Supporting Information, Figure S1).

The pristine P3HT reveals weak sensitivity of ~0.04 which suggests that blending nanoparticles is required to effectively inhibit the crystallization of polymer during spin coating. The sensitivity of P3HT/PC₇₁BM is much more significant than that of the P3HT/PC₆₁BM blend (0.67 vs 0.26). It is due to the easier intercalation of PC₇₁BM into P3HT crystallite than PC₆₁BM which has been reported elsewhere.²⁶ Specifically, the intercalation can effectively suppress the P3HT ordering during spin coating and thus induces significantly improved P3HT crystallinity upon VOC vapor exposure. However, the P3HT/Cu₂S and P3HT/TiO₂ reveal lower sensitivity (*S* = 0.07) and no sensitivity (*S* = 0.00), respectively, which can be speculated to the larger size of Cu₂S nanoparticles (5–6 nm) and TiO₂ nanorods (~20 nm). It implies that the larger nanocrystals are unable to intercalate into the P3HT crystallite but aggregate themselves into nanocrystal rich domains. Consequently, the excluded P3HT chains are confined within spaces left by nanocrystals, of which the polymer crystallinity is generally found to be enhanced when in a hybrid with inorganic nanocrystals.²⁷ Therefore, the degree for further improvement of crystallinity is limited, and hence, the lower sensitivity or even no sensitivity was obtained. In short, high sensitivity can be achieved in a conducting polymer/nanoparticles blend if the size of nanoparticles is small enough to intercalate with polymer crystallites and thus destruct the crystallinity of the as-spun film. All the above results evidence that the proposed methodology of VOC sensing is applicable and can be widely adopted in various blends or hybrid materials. In the following discussion, we will apply the P3HT/PC₆₁BM blend film to be the VOCs sensor because of the good performance, low cost, and easy access of PC₆₁BM.

The fabricated P3HT (60 kDa)/PCBM (PC₆₁BM) blend in 1:1 weight blending ratio deposited through 5000 r.p.m. is taken to sense a series of VOCs at their respective saturation vapor pressure with respect to different detection time. The

VOCs can be categorized according to their characteristic chemical structures, i.e., (1) aromatic hydrocarbons: toluene, *o*-xylene, *m*-xylene, *p*-xylene, chlorobenzene, and dichlorobenzene; (2) chlorinated aliphatic hydrocarbons: chloroform, dichloromethane, 1,2-dichloroethane, and tetrachloroethylene; (3) aliphatic hydrocarbons: *i*-pentane, *n*-hexane, *n*-octane, *n*-decane, and *n*-dodecane; (4) alcohols: methanol, ethanol, 1-propanol, and *n*-butanol; (5) others: acetaldehyde, acetone, and diethyl ether. They are all commonly used in industry and the laboratory. For example, *i*-pentane and toluene are the top two highest contents in gasoline, and tetrachloroethylene is a typical dry cleaning agent. Figure 2a–c shows the sensitivity with different exposure times to the vapor of chloroform and *i*-pentane, respectively, as representative examples in comparison with water.

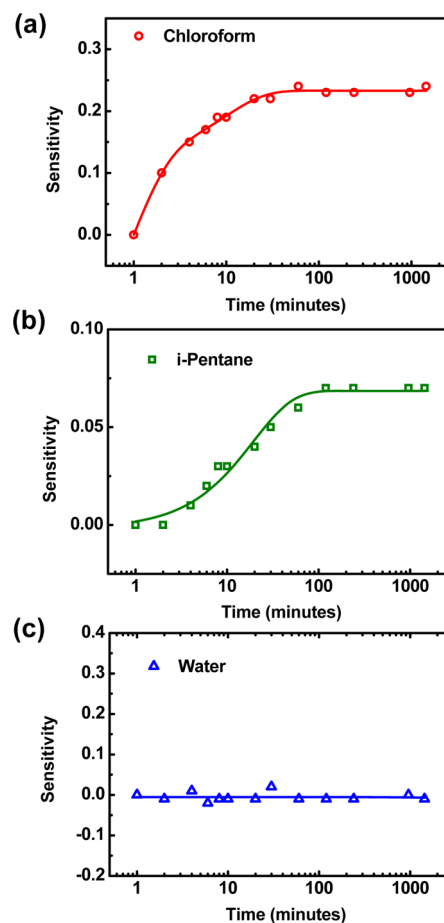


Figure 2. Sensitivity of P3HT/PCBM to VOCs of (a) chloroform and (b) *i*-pentane in comparison with (c) water for different exposure times. The solid lines represent the fitting curves of exponential increase for chloroform and *i*-pentane and constant for water.

For both chloroform and *i*-pentane, the P3HT/PCBM films respond quickly within the very early stage of exposure. This indicates that the warning can be delivered quickly within a few minutes which is extremely important for a real-time monitoring. The sensitivity is found to exponentially increase with exposure time and achieve a constant after exposure for ~100 min as the exponentially fitted curves shown in Figure 2a,b. A similar response of P3HT/PCBM to other VOCs (see Supporting Information, Figure S5), except water (Figure 2c) and alcohols (see Supporting Information, Figure S6), can be

also found. The results importantly suggest that the sensing would not be disrupted by water or other alcohols which commonly exist in the atmosphere. Consequently, the developed high performance sensor can be equipped under ambient atmosphere.

Table 2 summarizes the sensitivities S of all VOCs as well as the sensing errors σ of all selected VOCs. It can be observed

Table 2. Summary of Sensitivity, Saturation Vapor Pressure, Solubility of P3HT and PCBM of Different Volatile Organic Compounds (VOCs)

type of VOC	sensitivity	saturation vapor pressure (mmHg)	solubility of P3HT (mg/mL)	solubility of PCBM (mg/mL)
water	0.00 ± 0.02	24	0.0	0.0
methanol	0.02 ± 0.05	125	0.0	0.0
ethanol	0.02 ± 0.02	60	0.0	0.0
1-propanol	0.00	21	0.0	0.0
<i>n</i> -butanol	0.00	6	0.0	0.0
<i>i</i> -pentane	0.07 ± 0.02	532	0.0	0.0
<i>n</i> -hexane	0.08 ± 0.03	151	0.1	0.1
<i>n</i> -octane	0.17	14	0.1	0.1
<i>n</i> -decane	0.12	1	0.2	0.1
<i>n</i> -dodecane	0.04	0	0.2	0.1
toluene	0.20 ± 0.02	28	0.4	2.8
<i>o</i> -xylene	0.19	7	0.5	6.1
<i>m</i> -xylene	0.17	8	0.5	5.8
<i>p</i> -xylene	0.20	9	0.5	6.2
chlorobenzene	0.20 ± 0.01	12	45	7.0
dichlorobenzene	0.20 ± 0.02	1	37	27
chloroform	0.28 ± 0.02	194	26	16
dichloromethane	0.21	429	0.2	0.3
1,2-dichloroethane	0.13	79	0.0	2
tetrachloroethylene	0.22 ± 0.03	18	33	1.2
acetaldehyde	0.15 ± 0.06	903	0.0	0.0
acetone	0.07	231	0.0	0.1
diethyl ether	0.15 ± 0.03	534	0.0	0.0

that the sensing errors are lower than 14% (i.e., *i*-pentane) for all VOCs except the nonresponse water and alcohols. For the VOCs with high sensitivity such as chloroform, chlorobenzene, 1,2-dichlorobenzene, etc., the sensing errors are as low as 5% which suggests the reliable and accurate sensing. Additionally, it can be deduced that the sensitivity is closely correlated to the solubility of P3HT and PCBM in the VOCs. Therefore, in the present work, we quantify the solubilities of both molecules, respectively, by adding excess solids in each VOCs and separating the dissolved solution and undissolved precipitates by centrifugation. The pictures of centrifuged solution are shown in the Supporting Information, Figures S7 and S8. The determined solubilities are listed in Table 2 together with the saturation vapor pressures. From the table, we can clearly observe that the VOCs can be sensed if the VOCs can dissolve either P3HT or PCBM, even with considerably low solubility. For example, chloroform, chlorobenzene, 1,2-dichlorobenzene, etc., which are all toxic solvents, apparently show high sensitivity due to good solubility. Some VOCs that have selective solubility to P3HT and PCBM such as xylene can also be easily detected by the sensor. Interestingly, the VOCs with extremely low but not totally no solubility, such as *n*-hexane, *n*-octane, dichloromethane, etc., are all detectable which indicates the very powerful sensing capability of the sensor. It is also of

interest that, for *i*-pentane, acetaldehyde, and diethyl ether, which are all completely not a solvent for P3HT or PCBM, they can also be sensitized by the sensor. We speculate the results are due to the high saturation vapor pressure of these VOCs (>500 mmHg). Namely, the high saturation vapor acting as a lubricant enables the local movements of P3HT and PCBM molecules which can also lead to ordered structure and higher crystallinity. However, considering the water or alcohols, i.e., methanol, ethanol, 1-propanol, and *n*-butanol, the sensor is almost inert to these VOCs. In short, the sensor developed in the present work is powerful in accurately sensing VOCs which have solubility to P3HT or PCBM or have high saturation vapor pressure but without disruption of water or alcohols. This outcome can serve as a guide to determine if a molecule is detectable by this kind of sensor.

The detection limit of the sensor was tested with respect to various VOCs. The detection limit is defined as the lowest concentration of which the sensor can detect only when the sensitivity (S) is larger than two times of the sensing error (2σ). Table 3 lists the detection limit of 10 min sensing and 2 h

Table 3. Detection Limit of the P3HT/PCBM Sensor Exposed to Different VOCs Vapor for 10 min and 2 h, Respectively

VOCs	explosive limit (%)	detection limit 10 min (%)	detection limit 2 h (%)
<i>n</i> -octane	1.0	1.1	0.85
toluene	1.2	0.48	0.25
<i>o</i> -xylene	1.0	0.34	0.18
chlorobenzene	1.8	0.43	0.32
dichlorobenzene	2.0	0.13	0.03

sensing of selected toxic VOCs as well as their corresponding explosive limits. From the table, it can be observed that the explosive limits of the VOCs vapors can be detected by the sensor within 10 min which is thus able to promptly provide warnings of VOC exposure or leakage before explosion. These results further provide the evidence of the powerful capability of real-time monitoring in a high risk area of VOC leakage.

We finally constructed a setup to practically demonstrate the sensing ability of our developed VOC sensing materials as shown in Figure 3a. It includes a sensor box as shown in Figure 3b. For simplifying the demonstration, we used a single LED light source with wavelength of 650 nm which is close to the wavelength adopted in the sensitivity definition (600 nm). Note that the sensing procedure can be also performed by using a green light source with wavelength near 560 nm of which the absorption also changes significantly after VOCs exposure (cf. Figure 1). When the P3HT/PCBM sensing chip is exposed to the VOC vapor, the 650 nm LED light transmitted through the chip, i.e., detected by the photoresistor, would be considerably decreased due to the enhanced absorbance near 650 nm of P3HT/PCBM (Figure 1). The resultant resistance change in the circuit hence turns on the warning light to deliver alarm of VOCs exposure. It is noteworthy that all the components used in the setup cost less than 4 U.S. dollars (including the sensing chip, the circuit, and the LED light) which is much cheaper than any other commercially available VOC sensor. Furthermore, it is possible to reuse the raw materials by dissolving the polymer/nanoparticle thin films back to organic solvents and processing into new chips again. Therefore, the polymer/nanoparticle

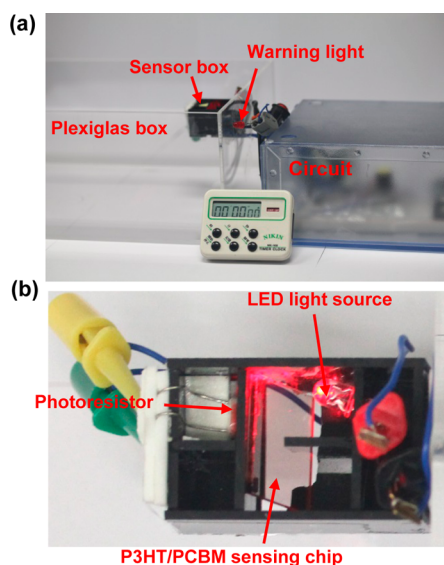


Figure 3. Pictures of (a) setup for performing real-time VOC sensing and (b) the sensor box. The sensor box composed of a P3HT/PCBM sensing chip, a LED light source with wavelength of 650 nm, and a photoreistor. The photoreistor is installed in a circuit with warning light and variable resistors as indicated in (a), and the detailed components in the circuit is shown in the Supporting Information, Figure S2. The sensor box is placed in a 6 L plexiglas box which is used to create the environment filling with VOC vapors at a controlled concentration. The real-time sensing procedure of toluene was recorded and is available through a Movie.

materials will not be wasted which would further decrease the cost.

A Movie recording the real-time VOC sensing of toluene vapor with concentration of explosive limits (1.2%, Table 3) was shot. We used toluene vapor to demonstrate the sensing procedure which has an explosive limit of 1.2%. We first created an environment filled with 1.2% toluene vapor by dropping 17.8 μL liquid toluene in a 6 L box (Figure 3 the transparent Plexiglas box) and waited for the liquid to completely evaporate. Afterward, we placed a P3HT/PCBM sensing chip into the sensor box. From the movie, it can be seen that, after the exposure of toluene vapor at around 4 min, the warning light started to flash continuously. It is still noteworthy that alarming in a time scale of minutes is still insufficient for real commercial validity. More investigations in materials design and processing adjustments are necessary in order to improve the sensitivity of the nanocomposite film and thus shorten the detection time down to the time scale of seconds. Nevertheless, herein, the demonstration of a practical sensing process still strongly indicates that our developed sensing materials and fabricated sensor device can alarm the dangerous VOCs in the surroundings. Our novel VOCs sensor hence shows the potential in extensive usage for safety and health protection of mankind in the near future.

CONCLUSIONS

In summary, we demonstrate a sensor adopting the proposed methodology that the optical property of conducting polymer/nanoparticles blend is sensitive to VOC vapor due to nanomorphological evolution and hence can be served as an indication of the presence of VOCs. This proposed methodology could be widely applicable to different blend or hybrid materials. The P3HT/PCBM served as a representative blend,

and the sensitivity of the P3HT/PCBM blend was optimized with respect to molecular weight of P3HT, P3HT/PCBM blending ratio, and spin rate of thin film deposition. A series of VOCs were chosen to test the applicability of the sensor, and the results reveal high performance without disruption by water and alcohols. The measurements of the detection limit show that the concentration over explosive limits can be detected by the sensor within several minutes. A real device adopting the developed sensing chip was fabricated, practically showing real-time sensing of VOCs in short time. The low cost, high sensitivity, high sensing accuracy, quick response, and real-time VOC sensor developed in the present work significantly extends the current VOC sensing technology and can be extensively used to effectively prevent humans and the environment from potential damages of VOCs.

ASSOCIATED CONTENT

Supporting Information

TEM images of TiO_2 nanorods and Cu_2S nanoparticles. Pictures and illustration of the sensor box and the circuit components. Schematic representation of P3HT/PCBM film morphologies before and after being exposed to solvent vapors. Relation between absorbance of P3HT/PCBM at the characteristic peak of 600 nm and the film thickness. Sensitivity with different exposure times with respect to various VOCs. Pictures of centrifuged solution of P3HT and PCBM, respectively, dissolved in various VOCs. This material is available free of charge via the Internet at <http://pubs.acs.org>

Web-Enhanced Feature

A movie of the real-time sensing procedure of toluene is available in the HTML version of the paper.

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Notes

The authors declare no competing financial interest.

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