A Low-Cost Miniaturized Colorimetric Sensor with Vertically-Stacked Semi-Transparent Finger-Type Organic Photo Detector for Formaldehyde Sensing

Ching-Fu Lin^a, Hsiao-Wen Zan^{a,*}, Chia-Jung Lu^{b,*}, Hsin-Fei Meng^c, and Olivier Soppera^{d,e}

^aDepartment of Photonics and Institute of Electro-Optical Engineering, College of Electrical and Computer Engineering, National Chiao Tung University, Hsinchu, Taiwan

^bDepartment of Chemistry, National Taiwan Normal University, Taipei, Taiwan

^cInstitute of Physics, National Chiao Tung University, Hsinchu, Taiwan

^d Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

^e Université de Strasbourg, France

*Email Address: hsiaowen@mail.nctu.edu.tw and cjlu@ntnu.edu.tw

Abstract

We proposed a sensitive colorimetric sensing system using a paper-like sensing layer on top of a vertically stacked finger-type organic photodetector (OPD) and commercial light-emitting diode (LED). The stacked OPD/LED device was small, with an area of 0.8 cm × 0.5 cm that was even smaller than a coin. Using commercial colorimetric formaldehyde (HCHO) sensing molecules to form the sensing layer, the stacked detecting system successfully detected HCHO of concentrations ranging from 40 to 1000 ppb within 20 min. Critical parameters affecting the sensitivity were investigated. The final system exhibited a stable calibration curve over 60 days. The long lifetime was attributed to using 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (PBDTTT-C-T) : phenyl-C71-butyric acid methyl ester (PC₇₁BM) to serve as a blended system and using the current variation ratio to represent the sensing response.

Keywords: colorimetric-type sensing; formaldehyde sensing; finger type; organic photodetector; vertically integrated

Introduction

Owing to the emergence of sensing technology in the Internet-of-things era, studies demonstrating low-cost and miniaturized sensor systems are increasing [1]. Gas sensors that detect toxic or explosive gas species attract significant attention because of their key applications in safety control and environmental monitoring [2-3]. To detect a target gas, several types of colorimetric probing molecules with high selectivity have been developed such as polyethylene-imine-protected copper nanoclusters for detecting trinitrotoluene (TNT), polydiacetylene for detecting dimethylformamide, and potassium disulfiteopalladate (II) ($K_2Pd(SO_3)_2$) for detecting carbon monoxide (CO) [4-6]. However, a low-cost, miniaturized, and sensitive color reading system has not yet been realized. Devadhasan et al. demonstrated color reading using mobile phones [7] that benefitted the development of handheld sensing systems. However, for environmental monitoring such as in a building or factory, we expect low-cost sensors to be used in several key positions such as at the inlets or outlets of gas flowing tubes or in critical contaminant areas. Hence, a concrete, low-cost, miniaturized, and sensitive color reading system is required.

In this study, to demonstrate the sensing ability of the proposed colorimetric sensing system, formaldehyde (HCHO) is chosen as the target gas. HCHO is a colorless, toxic, and carcinogenic volatile organic compound (VOC). It is widely used in indoor decorative materials, building materials, and paint; hence, it is a primary cause of the sick building syndrome (SBS) [8-9]. According to the report from the World Health Organization (WHO), in a 30-min exposure, the HCHO concentration should be below 82 parts-per-billion (ppb) [10]. Detecting HCHO in the ppb regime is hence highly required. Particularly, a real-time and low-cost detector is required for the general public to verify the safety of their surrounding environments. Colorimetric sensors using a sensing material that changes color when reacting with HCHO were proposed [11-22]. Hydroxylamine sulfate with pH indicator, 4-amino hydrazine-5-mercapto-1,2,4-triazole (AHMT), fluoral-P, and β -diketones have proven to be successful HCHO-sensing materials exhibiting high selectivity and ppb-regime sensitivity. Even though the colorimetric reaction is typically not reversible, low-cost reproducible test strips can be fabricated easily by casting the reacting material onto fibrous layers, such as papers, glasses, or films [11-14]. Identifying the color change using naked eye, however, is not reliable. In addition to using the conventional absorbance spectrometer, several groups have attempted to design low-cost and miniaturized systems to provide reliable color reading [15-22]. The most popular setup relies on a commercial light-emitting diode (LED) to irradiate the sensing film. The reflected light is collected by a commercial photodetector (PD), as shown in **Fig. 1(a)** [12, 15-17]. An alternative method consists of placing the LED on top, the PD at the bottom, and the sensing layer in between the LED and PD, as

shown in **Fig. 1(b)** [18-20]. However, the system is still bulky because the LED, sensing layer, and PD are positioned separately to form suitable light paths.

We herein propose a new design to realize a miniaturized, compact sensing system by vertically stacking the colorimetric sensing layer, semitransparent photodetector, and commercial LED. The semitransparent finger-type organic photodetector was used to allow the LED light to penetrate and detect the reflective light as the sensing signal. It is noteworthy that, in our previous work, we demonstrated such semitransparent OPDs to serve as proximity sensors [23]. In this study, we successfully verified that the detection of the reflective light can be used to perform sensitive colorimetric sensing. The proposed OPD utilized air-stable 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (PBDTTT-C-T): phenyl-C71-butyric acid methyl ester (PC₇₁BM) as the blended active layer. With glass encapsulation, the OPD exhibited a long lifetime (> 90 days) in air. By placing the finger-type OPD in between a commercial surface-mount device (SMD) LED and a fibrous-paper sensing film using AHMT as the HCHO colorimetric dye [25], the integrated system is even smaller than a US dime (**Fig. 1(c)**). Subsequently, the proposed integrated sensor is placed into a flow tube to detect HCHO in the ppb regime (**Fig. 1(d)**). A reliable and reproducible sensing calibration curve can be obtained for HCHO with concentration ranging from 40 to 1000 ppb. Moreover, even when the OPD has slightly decayed after 60 days, the sensor provides an almost unchanged sensing response when the current variation ratio is used instead of the current difference as the sensing parameter.

Fig. 1: (a) Conventional type-1, (b) conventional type-2, and (c) our proposed integrated design using a stacked fibrous sensing film, semitransparent finger-type OPD and SMD LED. (d) Integrated sensor in the flow tube.

2. Experimental setup

2.1 Materials

To fabricate the finger-type semi-transparent OPD, PBDTTT-C-T was purchased from Solarmer Energy Inc. and PC₇₁BM was obtained from UNI-ONWARD Corp.

To prepare the colorimetric HCHO-sensing paper, AHMT was purchased from Alfa Aesar Inc., potassium hydroxide (KOH) from Duksan Pure Chemicals Co., hydrochloric acid (HCl) from J.T. Baker Inc., and the porous glass filter used was Whatman GF/C.

2.2 Finger-type semi-transparent OPD fabrication

To fabricate the solution-processed finger-type semitransparent OPD that is shown in **Fig. 2(a)**, we first prepared a wet-etched indium tin oxide (ITO) glass substrate ($3\text{ cm} \times 3\text{ cm}$), which was cleaned by a standard cleaning method using acetone, isopropanol, and deionized water. After a 15 min UV ozone exposure process, we placed the ITO glass on a hot plate at $80\text{ }^{\circ}\text{C}$, and subsequently formed the blending active layer with PBDTTT-C-T and PC₇₁BM (**Fig. 1(c)**) by blade coating. Next, the specially designed finger-type aluminum electrode of width $60\text{ }\mu\text{m}$, interval 110 nm , and thickness 100 nm , was evaporated through a shadow mask by a thermal evaporator. Finally, this device was sealed with a UV adhesive glue in a glove box in which the water and oxygen concentrations were maintained below 0.1 ppm . The layer-by-layer device structure is shown in **Fig. 2(b)**.

For the active layer material, PBDTTT-C-T is a well-known polymer that typically acts as an electron donor and absorbs visible light well. PC₇₁BM is a material that can facilitate electron–hole separation, which plays an important role in enhancing the efficiency of photoinduced electron transfer. To prepare the PBDTTT-C-T:PC₇₁BM blending solution, we used a weight ratio 1:1.5 of PBDTTT-C-T:PC₇₁BM; subsequently, we dissolved the material in chlorobenzene ($2.25\text{ wt}\%$) and maintained the temperature at $60\text{ }^{\circ}\text{C}$ for 24 h until a thorough dissolution is achieved. Blade coating was used by depositing $30\text{ }\mu\text{L}$ of the active layer solution on the blade, after which the blade was moved at a fixed speed of 300 mm/s to form a 400-nm -thick active layer.

Fig. 2:(a) Fabrication process (b) Layer-by-layer structure of the finger-type OPD

2.3 Gaseous HCHO preparation

To prepare gaseous HCHO, we first used a microsyringe to draw formaldehyde solution (3.80-4.35 % W/V, in aqueous Phosphate Buffer, H121-08, Macron Fine Chemicals), which was subsequently injected into a 3 L Tedlar sealed bag filled with high-purity gaseous nitrogen. It is noted that the HCHO solution concentration is set to be 4% in the following calculation. After the HCHO solution had completely evaporated in the bag, gaseous HCHO was formed. The gaseous HCHO concentration was calculated as follows:

$$\rho = C \times \frac{101325}{P} \times \frac{273+T}{273} \times \frac{22.4}{M}, \quad (1)$$

where ρ is the HCHO concentration in ppm, C is the concentration of gaseous HCHO in mg/m^3 , P is the pressure in Pa, T is the temperature of the environment in $^{\circ}\text{C}$, and M is the molecular weight of HCHO. We used detector tube (10% RSD,

purchased from GASTEC Corp.) to confirm the HCHO concentration in Tedlar bag. This detector tube was calibrated by diffusion tube method according to manufacturer. As we used the detector tube to check the 16 ppm (calculated concentration was around 15.47 ~ 17.7 ppm) HCHO we prepared in Tedlar bag, the result showed 17 ± 1 ppm ($< 10\%$ RSD). This deviation is acceptable in this work for demonstrating the feasibility of HCHO sensing. If a calibration in ppb-regime is required, 2,4-dinitrophenylhydrazine-high performance liquid chromatography (DNPH-HPLC) method may be adopted [24].

2.4 Fabrication method of the colorimetric HCHO-sensing paper

To design a gaseous HCHO-sensing paper based on colorimetric detection, the selection of the sensing reagent is vital. Kawamura et al. demonstrated that an AHMT-based sensing design could achieve a higher color transformation rate compared to other traditional sensing designs, such as hydroxylamine-based sensing [12]. Therefore, in our work, we chose the method utilized by Kawamura et al. and prepared two types of reagent solutions. The first was 0.1 g AHMT dissolved in 9% HCl, and the other was 2.3 g KOH dissolved in 10 mL deionized water. The two reagent solutions were mixed in a volume ratio of 1:1, after which 100 μ L of the mixture solution was injected onto the Whatman GF/C glass filter paper to form the colorimetric sensing paper.

Dickinson et al. [25] demonstrated the principle behind the colorimetric HCHO sensing of AHMT, as follows: After AHMT (Fig. S1 (I)) reacts with HCHO, the formyl group of HCHO will form an intermediate (Fig. S1(II)), this intermediate should be unstable, and oxygen labile. Then, it will continuously turn quickly (< 1 min) to the final product 6-mercapto-s-triazolo[4,3-b] -s-tetrazine (Fig. S1(III)) between the liquid-air interface by aerial oxidation. This enables the color of the sensing solution to transform gradually from transparent to violet.

2.5 Formation of the vertically-integrated-type gaseous HCHO-sensing system

In our primary work, we designed a vertically integrated-type gaseous HCHO-sensing system using an AHMT colorimetric sensing paper for the HCHO reaction, a finger-type OPD for the electrical signal readout, and a commercialized 530 nm SMD LED chip for the light source. As shown in **Fig. 1(c)**, the size of the OPD is only 0.8 cm $\times$ 0.5 cm, which is similar to the size of the LED. With the special finger-type electrode design of the OPD, the light source can be integrated on the finger-type electrode side of the OPD, thus allowing light to partially pass through the

device. The OPD can subsequently detect the light reflected from the colorimetric sensing film. **Fig. 1(d)** illustrates the vertically integrated-type HCHO-sensing system and the gas-tight syringe with gaseous HCHO, which can be pumped using a stepper motor. The total gas flow rate was set at 1 L/min. As the pumping rate of the stepper motor is controlled by the ambient air dilution, the concentration of HCHO in the sensing chamber can be controlled. The colorimetric reaction between the AHMT paper and gaseous HCHO can change the reflection spectrum and hence vary the current signal in the OPD to provide a sensing signal proportional to the HCHO concentration.

It is noted that, if a high selectivity to HCHO is needed, choosing the wavelength as 540 nm is beneficial to improve the selectivity. This is because that AHMT reacts with different aldehyde materials to derivate different final products with different colors. The absorption spectrum changes among 520-555 nm. Choosing 540 nm, as reported by Kawamura et al. [12], delivers an improved selectivity to HCHO among various kinds of aldehyde such as acetaldehyde.

3. Results and discussion

3.1 Primary operation mechanisms of the vertically integrated-type gaseous HCHO-sensing system

The performance of the finger-type OPD is first evaluated. **Fig. S2(a), (b)** show the basic light/dark current performance and lifetime tracing result of the finger-type OPD used in this study, respectively. As show in **Fig. S2(a)**, the OPD performs well with a light/dark current ratio of approximately 10^5 at -1.5 V when a 10000 lux white light source is used. Furthermore, the OPD stably maintains a light/dark current ratio of 10^4 for over 90 days (**Fig. S2(b)**). This indicates that this OPD is both sensitive and reliable for applications related to light-intensity detection. Another characteristic of the OPD is its ultrasmall light-absorbing area ($0.2\text{ cm} \times 0.2\text{ cm}$). Therefore, this device can be easily sliced to a size suitable for embedding into systems for light-intensity detection. In this study, we sliced the OPD from its typical size of $3\text{ cm} \times 3\text{ cm}$ to $0.8\text{ cm} \times 0.5\text{ cm}$. Nevertheless, it maintained its light-intensity detection ability, as shown in **Fig. S2(c)**.

To build a gaseous HCHO-sensing system based on colorimetric sensing, we first performed a colorimetric sensing ability test on the AHMT filter paper. We set the glass filter on a glass substrate and used polytetrafluoroethylene tape to adhere both sides of the filter paper on the glass substrate, with the gas exposure area of $1.5\text{ cm} \times$

1 cm on the sensing chip. After depositing the AHMT sensing solution onto the filter paper, we moved the chip into the sensing chamber as in **Fig. 1(d)**, and subsequently commenced the colorimetric sensing evaluation test. **Fig. 3(a)** shows the color variation performance measured after 12 min of background air flow and 20 min gaseous HCHO flow. Similar to the color transformation of the solution, the sensing paper changed from white to violet when the HCHO concentration is greater than 150 ppb. However, it is difficult for the human eye to perceive this color change if the HCHO concentration is less than 90 ppb. Therefore, a tool that can detect the slight color change must be developed. Furthermore, the tool should be sufficiently small for portable applications. Embedding the finger-type OPD with an SMD LED may be an excellent solution owing to its high sensitivity when detecting reflective light.

To form the finger-type OPD HCHO-sensing system, we must consider a good match among three aspects: (1) reflectance spectrum of the sensing layer, (2) OPD absorption spectrum, and (3) luminance peak of the SMD LED. **Fig. 3(b)** shows the reflectance spectrum measured at the conditions given in **Fig. 3(a)**. As shown, the signal variation ranges from approximately 450 to 650 nm. Consequently, a commercial SMD LED with a luminance peak at 530 nm was chosen as the operating light source of the system. Notably, based on the absorbance spectrum of the active layer material of the OPD shown in **Fig. 3(c)**, this type of light can be well absorbed by the OPD. This suggests that the SMD LED is an appropriate choice for this system. We integrated the SMD LED with the OPD by embedding it at the bottom of the sensing chamber, as shown in **Fig. 1(d)**, to produce the vertically integrated-type HCHO-sensing system.

Regarding the sensing mechanism of the system, the AHMT paper serves as both the HCHO-sensing layer and the reflective surface for the OPD. Once the system detects HCHO, resulting in a color change in the paper, the reflective light intensity from the paper weakens owing to the variation in the reflectance value. This process can cause the output current of the OPD to decrease, thus allowing for the system to determine the precise gaseous HCHO concentration.

Fig. 3(d) shows the real-time OPD current tracing under gaseous HCHO flow detection with concentrations from 40 to 1000 ppb. The light source intensity was 35 W/m². It is noteworthy that the current difference, which is the current minus the initial current, is used in the y-axis to compare the current change under different HCHO concentrations. During each round of sensing, before injecting HCHO, air was flown in the background for 12 min until the background signal remained nearly constant. Subsequently, gaseous HCHO with a fixed concentration at a fixed flow rate of 1 L/min was injected for 20 min. As shown in **Fig. 3(d)**, when the HCHO concentration increases, the slope of the current difference increases as well. At a

fixed sensing time, the amount of current difference increases with the HCHO concentration. Even with 40 ppb HCHO, after 20 min, the current difference is apparent. This indicates that the sensitivity of the proposed sensing system may satisfy the safety exposure criterion set by WHO to detect 82 ppb within 30 min [3].

Fig. 3: (a) Color variation of AHMT paper after 12 min background air flow and 20 min gaseous HCHO flow (b) Corresponding reflectance spectrum comparison of AHMT paper measured after completion of HCHO flow (c) Absorbance spectrum of the active layer material of OPD (d) The current difference as a function of time when detecting HCHO ranging from 40 to 1000 ppb.

3.2 Discussion of the reliability and calibration method

To investigate the sensing behavior more carefully, the real-time sensing curve when detecting 90 ppb HCHO is shown in **Fig. 4(a)**. As previously mentioned, we first measured the background signal for 12 min, and subsequently inject 90 ppb HCHO for 20 min. It is observed that the background current remains nearly constant. When HCHO was injected, the current of the system decreased gradually. The test flow in **Fig. 4(a)** is set to be a standard flow for a single test. To evaluate the reproducibility and reliability of the sensing system, we used the vertically integrated sensing system to measure gaseous HCHO with concentrations ranging from 40 to 1000 ppb, all repeated thrice ($n = 3$). In every round of sensing, similar to the test

flow shown in **Fig. 4(a)**, we first measured the background signal for 12 min, and subsequently injected HCHO with a fixed concentration for 20 min. **Fig. 4(b)** shows the dynamic repeated test for 90 ppb HCHO. The measurements corresponding to other concentrations are shown in **Fig. S3**. In every test, a new AHMT sensing paper was used. In both **Fig. 4(b)** and **Fig. S3**, we obtained good repeated signals. Subsequently, we plotted the sensing response as a function of HCHO concentration to form the calibration curves.

In this study, two types of calibration curves were compared. The first one used the current difference and the second one used the current variation ratio to represent the sensing response. For the first type of calibration curve, as shown in **Fig. 4(c)**, the absolute value of the current difference ($-\Delta I$) at different sensing times (5, 10, 15, and 20 min) are plotted as a function of HCHO concentration. For the second type of calibration curve, we calculate the current variation ratio by dividing the absolute value of the current difference by the original current amount (I_0), as expressed by **Eq. (2)**.

$$\text{Current Variation Ratio} = \frac{-\Delta I}{I_0} \quad (2)$$

Subsequently, the current variation ratio with sensing times of 5, 10, 15, and 20 min are plotted as a function of HCHO concentration in **Fig. 4(d)**. In both **Figs. 4(c)** and **(d)**, the calibration curves exhibit greater sensing signals when the sensing time is increased. For a 20 min sensing time, the 40 ppb detecting signals can be clearly identified. For high HCHO concentrations such as 500 ppb or 1000 ppb, the system can deliver large sensing signals within 5 min.

Fig. 4: (a) Real-time current variation when detecting 90 ppb HCHO for 20 mins. (b) Repeated real-time measurement when detecting 90 ppb HCHO thrice using three different AHMT sensing papers. ($n = 3$, R : current variation ratio, M : mean value of sensing response, SD : standard deviation of sensing response) (c) Calibration curves using current difference as the sensing signal ($n = 3$). Sensing time varies from 0 to 20 min. (d) Calibration curves using current variation ratio as the sensing response ($n = 3$). Sensing time varies from 0 to 20 min.

3.3 Evaluating the long-term operation of the system

Although the vertically integrated HCHO-sensing system can detect low concentrations of HCHO, the lifetime performance of the system cannot be neglected. In this study, the calibration curves using current difference and current variation ratio as sensing signals were compared. **Fig. 5(a)** shows the current difference when detecting 70 ppb HCHO at days 6 and 60. Obviously, the current difference decreases significantly at day 60. This phenomenon indicates that the sensitivity of the OPD to light intensity variation decays gradually with time. As shown in **Fig. S4**, even though the fabricated OPD exhibits a good light/dark current ratio over 90 days, the output current at -1.5 V decreases from $\sim 8 \times 10^{-6}$ A to $\sim 4 \times 10^{-6}$ A from day 6 to day 60. Consequently, using current difference to serve as the sensing signal results in degradation with time. However, if we use the current variation ratio to serve as the

sensing response, a rather stable calibration curve can be obtained even after 60 days, as shown in **Fig. 5(b)**. Therefore, the sensing response analysis method is more appropriate for prolonging the operating lifetime of this vertically integrated HCHO-sensing system.

Fig. 5: 70 ppb HCHO real-time sensing curves using (a) current difference and (b) current variation ratio to represent the sensing signal, at days 6 and 60.

3.4 Improving sensitivity by increasing light intensity

As previously mentioned, the vertically integrated HCHO-sensing system can successfully detect HCHO as low as 40 ppb. To further enhance the sensing signal to ppb-regime detection, increasing the light intensity is an effective method. With an irradiance of 35 W/m^2 and 65 W/m^2 , the current difference and current variation ratio are plotted as a function of HCHO concentration in **Figs. 6(a)** and **6(b)**, respectively. Increasing light intensity can significantly enlarge the sensing signal. Specifically, when detecting 40 ppb HCHO for 20 min, the current difference increases from $4.1 \times 10^{-8} \text{ A}$ to $1.7 \times 10^{-8} \text{ A}$ when increasing the light irradiance from 35 W/m^2 and 65 W/m^2 . With the same condition, the current variation ratio increases from 0.6% to 1.4%. This verifies that, given a light source with suitable intensity, this vertically integrated gaseous HCHO-sensing system can detect HCHO in the ppb regime.

Fig. 6: (a) Current difference and (b) sensing response plotted as a function of HCHO concentration with light intensities of 35 W/m² and 65 W/m² (n = 3).

4. Conclusion

In this study, we successfully demonstrated a sensitive colorimetric sensing system using a paper-like colorimetric HCHO-sensing layer on top of a vertically stacked semitransparent OPD and commercial SMD LED. The area of the miniaturized stacked OPD/LED device was only 0.8 cm × 0.5 cm, which was suitable for developing portable or wide-spread sensing devices. When HCHO reacted with the sensing layer to cause a color change, the OPD/LED system detected the reflectance light of the sensing layer. For HCHO lower than 90 ppb, the color change cannot be identified easily by the human eyes, but the system successfully delivered a reliable current change to serve as the sensing signal. We confirmed the repeatability and the reliability of the proposed sensing system. Furthermore, we noticed that using current variation ratio instead of the current difference to serve as the sensing response improved the system lifetime significantly to longer than 60 days. Increasing the LED light intensity enhanced the sensitivity in low-concentration HCHO. The stacked system successfully detected HCHO of concentration ranging from 40 to 1000 ppb within 20 min; this satisfied the requirement of WHO. In future, considering real applications, pushing the HCHO detection limit to be less than 10 ppb is beneficial to further improve the sensing accuracy. Possible methods include enhancing the light/dark current ratio of the OPD to enlarge the sensing dynamic range and forming a HCHO sensing film with higher sensitivity. According to literatures, coating the sensing reagent on substrates with nanostructures such as silica porous substrate [20] or electrospinning fibrous film [13] may increase the gas reacting area and hence the sensitivity. Moreover, in addition to HCHO sensing, we expect the proposed semitransparent OPD/LED system to be easily integrated with other colorimetric chemical sensing films to provide sensitive color-reading.

Acknowledgements

This work was supported by the Ministry of Science and Technology (MOST), Taiwan (Project number 107-2221-E-009 -086), and by MOST Add-on Grant for International Cooperation (Project number 108-2923-E-009 -002 -MY3).

References

- [1] R. Baron & J. Saffell., Amperometric gas sensors as a low cost emerging technology platform for air quality monitoring applications: A review. *ACS sensors*, 2(11), 1553-1566. 2017.
- [2] R. N. Gillanders, I. D. Samuel & G. A. Turnbull., A low-cost, portable optical explosive-vapour sensor. *Sensors and Actuators B: Chemical*, 245, 334-340. 2017.
- [3] B. Urasinska-Wojcik, T. A. Vincent, M. F. Chowdhury & J. W. Gardner., Ultrasensitive WO₃ gas sensors for NO₂ detection in air and low oxygen environment. *Sensors and Actuators B: Chemical*, 239, 1051-1059. 2017.
- [4] R. S. Aparna, J. A. Devi, P. Sachidanandan & S. George., Polyethylene imine capped copper nanoclusters-fluorescent and colorimetric onsite sensor for the trace level detection of TNT. *Sensors and Actuators B: Chemical*, 254, 811-819. 2018.
- [5] T. Wang, Y. Guo, P. Wan, X. Sun, H. Zhang, Z. Yu & X. Chen., A flexible transparent colorimetric wrist strap sensor. *Nanoscale*, 9(2), 869-874. 2017.
- [6] C. Lin, X. Xian, X. Qin, D. Wang, F. Tsow, E. Forzani & N. Tao., High Performance Colorimetric Carbon Monoxide Sensor for Continuous Personal Exposure Monitoring. *ACS sensors*, 3(2), 327-333. 2018.
- [7] J. P. Devadhasan, D. Kim & S. Kim., Smartphone coupled handheld array reader for real-time toxic gas detection. *Analytica chimica acta*, 984, 168-176. 2017.
- [8] W. J. Kim, N. Terada, T. Nomura, R. Takahashi, S. D. Lee, J. H. Park & A. Konno., Effect of formaldehyde on the expression of adhesion molecules in nasal microvascular endothelial cells: the role of formaldehyde in the pathogenesis of sick building syndrome. *Clinical & Experimental Allergy*, 32(2), 287-295. 2002.
- [9] B. Sahlberg, M. Gunnbjörnsdottir, A. Soon, R. Jogi, T. Gislason, G. Wieslander, & D. Norback., Airborne molds and bacteria, microbial volatile organic compounds (MVOC), plasticizers and formaldehyde in dwellings in three North European cities in relation to sick building syndrome (SBS). *Science of the total environment*, 444, 433-440. 2013.
- [10] A. Allouch, M. Guglielmino, P. Bernhardt, C. A. Serra, & S. Le Calvé., Transportable, fast and high sensitive near real-time analyzers: formaldehyde

- detection. *Sensors and Actuators B: Chemical*, 181, 551-558. 2013.
- [11] X. Wang, Y. Si, J. Wang, B. Ding, J. Yu & S. S. Al-Deyab., A facile and highly sensitive colorimetric sensor for the detection of formaldehyde based on electro-spinning/netting nano-fiber/nets. *Sensors and Actuators B: Chemical*, 163(1), 186-193. 2012.
- [12] K. Kawamura, K. Kerman, M. Fujihara, N. Nagatani, T. Hashiba & E. Tamiya., Development of a novel hand-held formaldehyde gas sensor for the rapid detection of sick building syndrome. *Sensors and Actuators B: Chemical*, 105(2), 495-501. 2005.
- [13] X. Wang, Y. Si, X. Mao, Y. Li, J. Yu, H. Wang & B. Ding., Colorimetric sensor strips for formaldehyde assay utilizing fluoral-p decorated polyacrylonitrile nanofibrous membranes. *Analyst*, 138(17), 5129-5136. 2013.
- [14] Y. Y. Maruo, J. Nakamura & M. Uchiyama., Development of formaldehyde sensing element using porous glass impregnated with β -diketone. *Talanta*, 74(5), 1141-1147. 2008.
- [15] N. Nakano & K. Nagashima., An automatic monitor of formaldehyde in air by a monitoring tape method. *Journal of Environmental Monitoring*, 1(3), 255-258. 1999.
- [16] Y. Suzuki, N. Nakano & K. Suzuki., Portable sick house syndrome gas monitoring system based on novel colorimetric reagents for the highly selective and sensitive detection of formaldehyde. *Environmental science & technology*, 37(24), 5695-5700. 2003.
- [17] M. N. Descamps, T. Bordy, J. Hue, S. Mariano, G. Nonglaton, E. Schultz & S. Vignoud-Despond., Real-time detection of formaldehyde by a fluorescence-based sensor. *Procedia Engineering*, 5, 1009-1012. 2010.
- [18] K. Toda, K. I. Yoshioka, K. Mori, & S. Hirata. Portable system for near-real time measurement of gaseous formaldehyde by means of parallel scrubber stopped-flow absorptiometry. *Analytica Chimica Acta*, 531(1), 41-49. 2005.
- [19] Q. Meng, T. Han, G. Wang, N. Zheng, C. Cao & S. Xie., Preparation of a natural dye doped Ormosil coating for the detection of formaldehyde in the optical gas sensor. *Sensors and Actuators B: Chemical*, 196, 238-244. 2014.
- [20] X. Qin, R. Wang, F. Tsow, E. Forzani, X. Xian & N. Tao., A colorimetric chemical sensing platform for real-time monitoring of indoor formaldehyde. *IEEE Sensors Journal*, 15(3), 1545-1551. 2015.
- [21] J. Li, C. Hou, D. Huo, M. Yang, H. B. Fa & P. Yang., Development of a colorimetric sensor array for the discrimination of aldehydes. *Sensors and Actuators B: Chemical*, 196, 10-17. 2014.
- [22] Y. Sekine, R. Katori, Y. Tsuda & T. Kitahara., Colorimetric monitoring of

formaldehyde in indoor environment using built-in camera on mobile phone.

Environmental technology, 37(13), 1647-1655. 2016.

- [23] C.H. Chen, C.F. Lin, K.H. Wang, H.C. Liu, H.W. Zan, H.F. Meng, W. Hortschitz, H. Steiner, A. Kainz, T. Sauter, Organic Electronics, 49, 305-312, (2017)
- [24] R. W. Gillett, H. Kreibich & G. P. Ayers., Measurement of indoor formaldehyde concentrations with a passive sampler. Environmental science & technology, 34(10), 2051-2056. 2000.
- [25] R. G. Dickinson & N. W. Jacobsen., A new sensitive and specific test for the detection of aldehydes: formation of 6-mercapto-3-substituted-s-triazolo [4, 3-b]-s-tetrazines. Journal of the Chemical Society D: Chemical Communications, (24), 1719-1720.1970.

Supporting information

Fig.S1: AHMT-formaldehyde reaction process and structure transformation

(c)

Fig. S2:(a) OPD light/dark current performance measured by sweeping voltage from -1.5 V to 1.5 V (b) OPD light/dark current performance measured by fixed bias voltage -1.5 V (c) Basic light/dark current comparison with different OPD sizes

Fig.S3: repeated formaldehyde measurement corresponding to (a) 0 ppb (b) 40 ppb (c) 70 ppb (d) 150 ppb (e) 500 ppb (f)1000 ppb

Fig.S4: Background output current comparison between day 6 and day 60