METHANOL DETECTION BY A MWCNT/PEDOT:PSS NANOCOMPOSITE SENSOR

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Abstract: In this paper, the sensing properties of multi-walled carbon nanotubes (MWCNT) and conductive polymer mixture poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) nanocomposites towards methanol vapor were measured at room temperature. The proposed MWCNT/PEDOT:PSS sensors were fabricated by coating different volumes of the dispersions on the polyethylene terephthalate (PET) flexible substrate to produce different film thicknesses. The substrate was already coated with screen-printed silver interdigitated electrodes. Compared with MWCNT films, the proposed composite films significantly showed a higher response toward methanol vapor. The thinnest film with only 5 µL drop casted dispersion has shown the best response, 27.62% change in resistance at 70 ppm.

Keywords: MWCNT, PEDOT:PSS, nanocomposites, VOCs sensor, Methanol

1. Introduction

With the development of the Internet of Things (IoT), the role of gas sensors is gradually becoming more prominent [1-2]. The demand for gas sensors grew alongside with IoT and sparked even by COVID 19 pandemic [3]. Gas sensors can be employed to prevent early gas leakage [4], monitor in- or outdoor air quality [5], diagnose diseases [6], and others [7], which play important role in daily life and industrial production. Volatile organic compounds (VOCs), such as methanol vapor is reported to be a harmful compound for human beings, causing adverse symptoms such as skin itching, vision impairment, poisoning, and coma [8]. Human can be exposed for example to methanol which even occurs in the human body itself as well as can come from different sources in food, drink, and fuels [9]. Therefore, it is necessary to monitor the concentration of methanol vapor in an indoor or industrial environment.

Traditional metal oxide-based sensors are capable to detect methanol vapor at ppb level, but still, demonstrate disadvantages such as low selectivity and high operating temperatures (typically 300-500°C) [10-12]. The sensing principle of these sensors is based on the chemical oxidation or reduction reactions between oxygen ions and the measured gas, but high temperature is a necessary condition to produce oxygen ions [11], which increases power consumption and reduces the chances for these sensors to be implemented in a portable solution.

Carbon nanotubes (CNTs) [12-13] and other carbon-based nanomaterials [14-15] are the most widely used sensitive material for gas sensors. Their large specific surface area, excellent adsorption capacity, and special electrical properties [16] have shown great potential in the field of gas sensing. In [12,17-18] it was shown that mixing CNTs with metal and metal oxide nanoparticles (NPs) enhances the gas detection performance. Composites of CNTs and conductive polymers are promising for gas and VOCs detection [19-21]. Several studies reported that composites of CNTs with conductive polymer (CPs) [22-24] or metal oxide [25-26] can be employed for the detection of methanol.

Due to the porous and fibrous surface structure and excellent conductivity, CPs offer a large effective surface area, i.e. larger adsorption surface, which shows high potential as sensing materials for VOCs sensors at room temperature [27]. CPs-based VOCs sensors can detect low-level analytes [28]. PEDOT: PSS is a popular polymer mixture of two monomers, which shows high conductivity [29]. In [30] its effectiveness in methanol detection has been proven.

In this paper, we investigate the sensing properties of sensors based on MWCNT as well as MWCNT/PEDOT:PSS films toward methanol vapor at low ppm concentration by tuning the dispersed volume of the nanocomposite materials.

2. Material and methods

Hydroxyl group functionalized multi-walled carbon nanotube (MWCNT-COOH) was dispersed in 1% sodium dodecylbenzene sulfonate (SDBS) and sonicated at 30% power (max. 20 W) for 30 minutes by ultrasonication probe. MWCNT/PEDOT:PSS (0.1% MWCNT) composite

was also prepared by ultrasonication in the same manner, following previous work and after trial experiments [31]. Different volumes of both dispersions (5 µl, 10 µl, 15 µl, 20 µl) were drop-casted onto screen-printed silver interdigitated electrodes on PET substrate to fabricate sensors.

UV-vis-NIR spectroscopy was carried out for the dispersions quality check by using Cary 60 Spectrophotometer (Agilent Technologies, CA, USA).

The proposed sensors were measured under a methanol vapor environment generated by a VOC generator OVG-4 VOC gas generator device manufactured by Owlstone Inc., USA. A mass flow controller with LabVIEW interface was used to control methanol vapor at concentrations in the range of 10-70 ppm. The response of sensors was collected by measurement of the resistance of the sensors ny the data acquisition system DAQ970A equipped with DAQM900 multiplexer (Keysight Technologies, CA, USA). The measurement setup is shown in Figure 1. The relative change of the resistance is shown for the comparison between the reference nitrogen condition and the different methanol concentrations as per equation (1):

$$\frac{\Delta R}{R}\% = \frac{R_i - R_0}{R_0}\% \qquad (1)$$

where R_i is the resistance of the sensor at a certain ppm of methanol and R_0 is the initial resistance in nitrogen at the beginning of the measurement. Nitrogen was used as career inert gas to avoid the effect of air and other composites such as oxygen or carbon dioxide. Response and recovery times were obtained by alternating the gas flow between 10 and 70 ppm automatically by LabVIEW, controlling the mass flow controllers, where they were calculated at 63 % and 90% of the final value of the resistance.

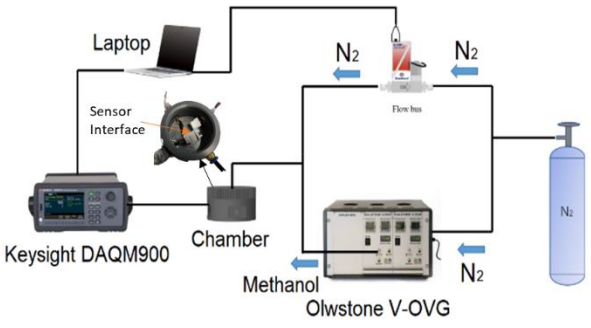


Figure 1: Schematic of the VOCs control system in measurement

3. Results and discussion

MWCNT which was directly dispersed in deionized water is very poor where the agglomeration is visibly observable. In comparison, MWCNT/PEDOT:PSS and MWCNT/SDBS solutions have clear dispersion without observed agglomerations. Figure 2 shows the UV-vis-NIR absorption spectra of the three MWCNT dispersions. The difference in absorbance peak at ~300 nm is apparent for those dispersions compared with SDBS or PEDOT:PSS. It can be indicated that SDBS has the best dispersion effect on carbon nanotubes, followed by PEDOT:PSS, while deionized water has not worked effectively to disperse the carboxylic functionalized MWCNT.

Four different MWCNT/SDBS sensors are placed in a chamber and the response of the sensors to methanol gas from 10-70 ppm was measured. In Figure 3, it can be seen that the responses of different casted films of MWCNT/SDBS to methanol gas do not show particular changes by increasing methanol concentration. This is because the carbon nanotubes themselves only show a certain response to strong oxidizing or strong reducing gases, and the response-ability to weakly reducing gases such as methanol is not outstanding.

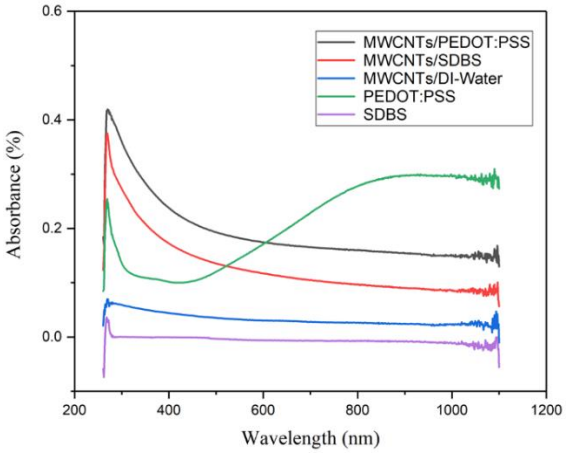


Figure 2: UV-vis-NIR spectra of proposed composites in comparison to as-received PEDOT:PSS and the SDBS aqueous solution

In the same way, the response of different films of PEDOT:PSS/MWCNT sensors for 10-70 ppm methanol gas was measured. Figure 4 shows that the response of MWCNT/PEDOT:PSS was greatly optimized for methanol compared to MWCNT/SDBS (Figure 3), and it can be seen from the figure that a dispersed 5 µl volume of MWCNT/PEDOT:PSS shows the best response compared to other dosages, and the response of 5 µl, 10 µl, and 15 µl of MWCNT/PEDOT:PSS in a methanol environment at 70 ppm was 27.62%, 26.16%, and 24.12%, respectively. It should be noted that the response curve of 20 µl of MWCNT/PEDOT:PSS was distorted due to the small film resistance, and the response did not continue to improve with the increase of gas concentration after 40 ppm.

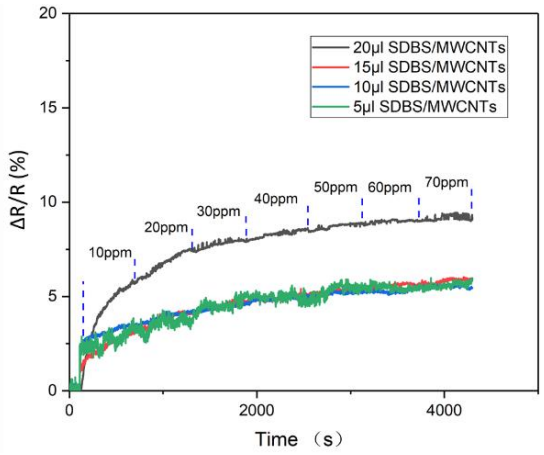


Figure 3: Response of MWCNT/SDBS sensors with different deposition volumes toward methanol vapor at 10 – 70 ppm

The original PEDOT:PSS film showed a very smooth surface, then became rough after adding carbon nanotubes. There are two and many nano-scale protrusions. These protrusions are polygonal in shape, and can significantly enhance the adsorption capacity of the composite material. And hence the active surface area. The conductivity of carbon graphene structure increases by more than two times after adding PEDOT:PSS to graphene. The mixing of the two materials dramatically increases the ability of charge transport, which can increase the gas sensitivity of the material to a particular extent characteristic [32]. Methanol can lead to the increase of MWNT/PEDOT:PSS conductivity by increasing the wettability at the contact between the CNT and the polymer [33]

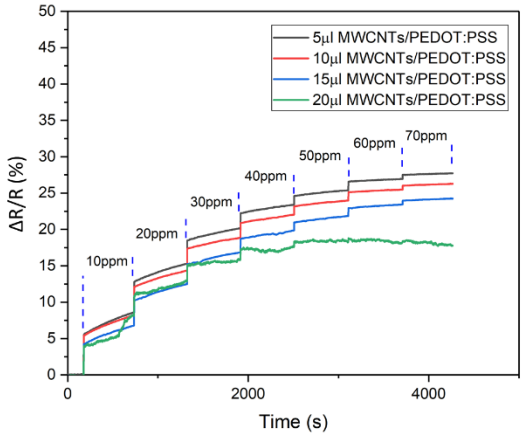


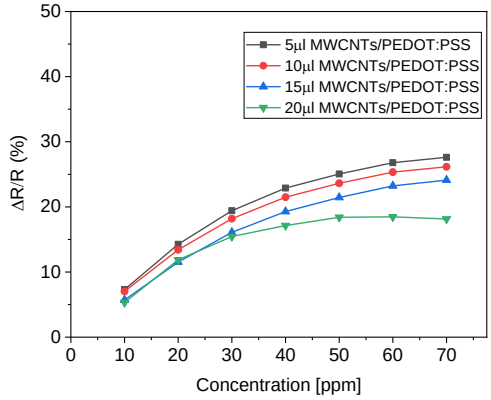
Figure 4: Response of MWCNT/PEDOT:PSS sensors with different deposited volumes toward methanol

The response time and recovery time were analyzed for 5 µl PEDOT:PSS/MWCNTs between 0-70 ppm methanol gas environment, as shown in Figure 5b. Both response time and recovery time were calculated for T_{63} and T_{90}. It was found that the response time is T_{63}=5 s, T_{90}=44 s, and the recovery time T_{63}=7 s, T_{90}=9 s. It can be seen that the sensor of PEDOT:PSS/MWCNTs composite has a fast response time and recovery time at room temperature. In comparison with literature [34], for measurement at room temperature, the proposed sensor outperforms several materials with a detection level at 10 ppm, much less than the permissible exposure limit of 200 ppm [ref], and fast response and recovery time.

4. Summary

MWCNT/PEDOT:PSS and MWCNT/SDBS formed good dispersions. However, the conductivity of PEDOT:PSS is higher regardless that MWCNT/SDBS show higher quality dispersion. MWCNT/PEDOT:PSS was sensitive to methanol even in a very low ppm concentration of 10 ppm. The lower the film thickness (lesser dispersed volume of the materials on the substrate), the higher the sensitivity. For 5 µl film, the response reached 27.6% at the concentration of 70 ppm and it has good repeatability (Figure5). The sensor has also fast response and recovery times.

a)



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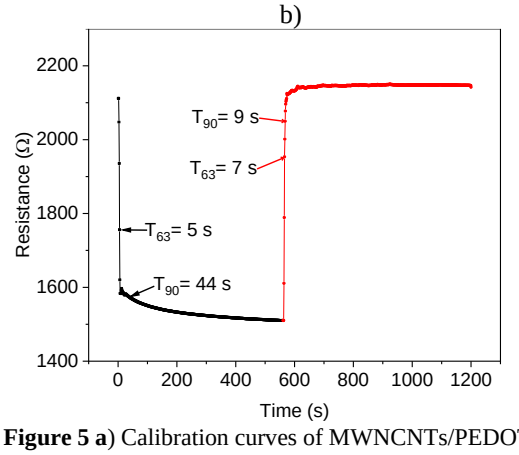

Figure 5 a) Calibration curves of MWNCNTs/PEDOT:PSS films and b) response and recovery time of 5µl PEDOT:PSS/MWCNTs

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