# RAPID DETECTION OF TRACE OZONE BY USING SWCNT-IN2O3 MATERIALS

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**Abstract** - In this study, the sensitivity of SWCNT-$In_2O_3$ materials to trace ozone (from 20 ppb to 2.4 ppm) was investigated at room temperature. The SWCNT-$In_2O_3$ materials were characterized using X-ray diffraction and Raman spectroscopy. The sensing properties of various ratios of SWCNT-$In_2O_3$ were measured. Among the various weight ratios of SWCNT-$In_2O_3$, the sensor response of the 2.0 wt% SWCNT-$In_2O_3$ was the highest obtained response (13.21) to 1500 ppb ozone. The ozone sensing properties are attributed to the mechanism of adsorption, desorption, and the surface reaction processes of ozone. Therefore, the SWCNT-$In_2O_3$ has potential and promising application in the field of ozone detection.

**Index Terms** - SWCNT-$In_2O_3$; ozone; sensing properties; sensing mechanism.

## I. INTRODUCTION

Ozone is a triatomic molecule, consisting of three oxygen atoms. Ozoneis a useful oxidation agent that has numerous useful industrial and consumer applications,such as drinking water pretreatment, wastewater treatment,chemical processes,food sanitation and storage, purification of gases, air deodorizing and so on [1–3].

However, ozone is powerful oxidizing reagent and its appearancein the ambient atmosphere is very harmful for human health, as it causes headache, burning eyes, respiratory irritation, and lung damage. For example, exposure of 0.1 ppm ozone continuously for two hours causes a decrease in spirometric lung function (a loss of 20% in breathing capacity) [4]. Therefore, thewidespread use of ozone has created a strong demand for a highly sensitive, simple method for monitoring the concentration of ozone in the atmosphere under various conditions. Various analytical methods have been employed to determine ozone concentrations, such as amperometric, optical, resistive, impedance spectroscopic, reversible photoreductive, fluorescent, chemiluminescent, high-performance liquid chromatography-mass spectrometry (HPLC-MS), electrochemical, colorimetric methods and so on [5–18].

Among these methods, sensors based on metal oxide semiconductor have several advantages for detecting ozone concentrations, such as high sensitivity, stability, short response time, low cost, low weight, low energy consumption and low working temperature [19]. Different metal oxide semiconductor materials have been studied for their potential application as ozone gas sensors[20–24]. For instance, n-type materials such as indium oxide ($In_2O_3$) [25] and tungsten trioxide ($WO_3$) [26] have received a great deal of attention during the past few years. It has been found that nanostructured $In_2O_3$-based conductometric thin film gas sensor with high sensitivity and selectivity to ozone. In particular, the gas-sensing performance of $In_2O_3$-based gas sensor can be improved significantly by surface chemical modification [27]. To the best of our knowledge, there are no studies about the sensitivity of SWCNT-$In_2O_3$ to ozone. To fill this gap, the purpose of this research is to develop a novel ozone sensor based on SWCNT-$In_2O_3$for detection of trace amount of ozone at room temperature. The structures of SWCNT-$In_2O_3$ has been characterized by X-ray diffraction and Raman spectroscopy. We also study the mechanism of the gas sensing response and use electrical characterization to check the sensitivity and stability of the SWCNT-$In_2O_3$sensor to ozone.

## II. EXPERIMENTAL

### A. Preparation of SWCNT-$In_2O_3$

All the chemicals used in this study are of analytical reagent grade, and are purchased from Alfa Aesar Chemical Co., Inc. (USA). Water was distilled and deionized using a Milli-Q water purification system (Millipore Corp.).The SWCNT powders were slowly added into the aqueous ethanol solution with $In_2O_3$ content of 0.2, 0.5, 1.0, and 2.0 wt% with constant stirring for 1 h at room temperature and subsequently evaporated the solvent. Finally, the samples were calcined at 400℃ for 2 h in air to obtain the SWCNT powders coated with various content of In2O3.

### B. Characterization of SWCNT-$In_2O_3$

The characterization of the crystal structures of the SWCNT-$In_2O_3$ was carried out by a XRD-6000 Shimadzu X-RAY Diffractometer, with Cu Kα radiation at 40 keV and 30 mA between 10º and 80º (2θ) with 2º/min. The Raman spectra of SWCNT-$In_2O_3$ were collected using a Raman microspectrometer (ENWAVE EZRaman-xB) in the spectral range 250-2350 $cm^{-1}$.

### C. Sensor fabrication

A sensing material was fabricated by mixing the prepared sample and 5 wt% polyvinyl alcohol, which was added as a binder. The sensing films were fabricated by dip coating it on a pair of comb-like gold electrodes existing on an alumina substrate with dimensions of 10 mm×5 mm. The sensing films were heated at 100 ℃ for 1 h, and calcined at 400 ℃ for 2 h.

### D. Sensing system

The ozone response measurement was conducted in a dynamic flow system, in which the sensors were housed in a glass cover chamber, as shown in Figure 1. The diameter of the glass cover (gas sensing chamber) is 12.3 cm. The ozone gas was produced by an ozone generator (TCA 158, Tsun Cheng Co., Taiwan) and was diluted with air to 15-3580 ppb by adjusting two mass flow controller, which was monitored by a commercial ozone sensor (MIL-RAM 01-2313). The ozone gas was produced by an ozone generator (TCA 158, TsunCheng Co., Taiwan) in this sensing system. The total flow rate of the testing gas (ozone/air) was fixed at 400 cm3/min during measurements and the temperature of the sensor device was controlled at 25 ± 2 ℃, with the humidity maintained at 50 ± 5 % RH. The sensor response (S) was defined as $S = R_{ozone}/R_{air}$, where $R_{ozone}$ is the electrical resistance of the sensor in ozone gas, and $R_{air}$ is the electrical resistance in the air. The response time (t90) is defined as the time taken to go from 10 to 90% saturation value, while the recovery time (tr90) is the reverse of the response time. Other gas inference tests were performed under the same conditions. Interference gases of 1500 ppb CO, 1500 ppb NH3, 1500 ppb NO and 1500 ppb H2 were employed for the sensing system. The sensor response to reducing gas and oxidizing gas were defined as S1 = Rair/Rreducing gas and S2 = Roxidizing gas/Rair, respectively, where Rreducing gas is the electrical resistance of the sensor in reducing gas, and Roxidizing gas is the electrical resistance of the sensor in oxidizing gas.

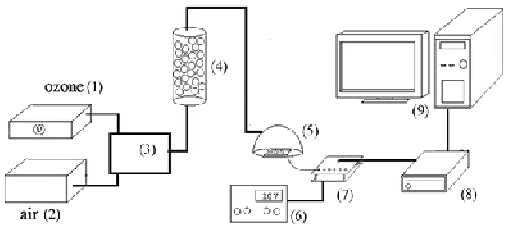



**Figure 1. Ozone detection laboratory equipment diagram. (1) ozone generator, (2) gas pump, (3) mass flow controller, (4) drying tube, (5) plastic chamber, (6) power supply, (7) commercial ozone sensor, (8) data acquisition system, (9) computer.**

The sensor process of the interference tests were the same as the ozone gas condition. All electrical resistance measurements were performed using a Jiehan 5000 data acquisition system, a simple voltage circuit was used to measure the sensor resistance with an input voltage of 2 V, and a computer was used to perform data acquisition and processing. The condition of the signal measurements is with input voltage 1 V and frequency 1 kHz.

## III. RESULTS AND DISCUSSION

### A. Structure characterization

As shown in Figure 2, the peaks corresponding to (211), (222), (400), (431), (440) and (622) crystal planes, respectively, which can be indexed to cubic indium oxide (JCPDS file no. 06-0416) [28]. Meanwhile, no other crystalline phase is observed in all the diffraction patterns, indicating that some indium oxide ($In_2O_3$) nanofibers may form on the surface of SWCNT.

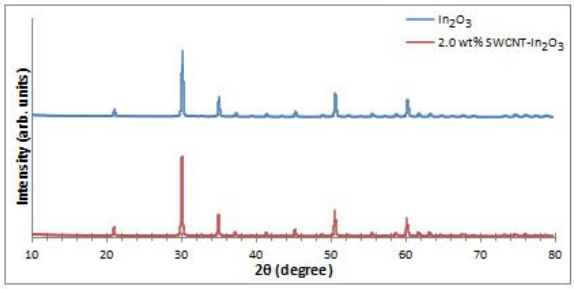



**Figure 2. XRD patterns of $In_2O_3$ and 2.0 wt% SWCNT-$In_2O_3$.**

To further examine the different crystalline structures of the SWCNT-$In_2O_3$, Raman spectroscopy measurements were performed on the samples, as illustrated in Figure 3. The recorded spectrum of In2O3 shows five strong Raman bands are discernible, which correspond well to the band positions of $In_2O_3$, as reported in the literature [29]. Contrary to $In_2O_3$, Raman spectrum is recorded in the spectral range of the SWCNT-$In_2O_3$ with two different Raman bands at about 1350 cm-1 and 1582 cm-1, which are characteristic peaks of the D and G bands from SWCNT [30]. Meanwile, the intensity ratios of the Raman D and G bands indicates the high quality of the SWCNT.

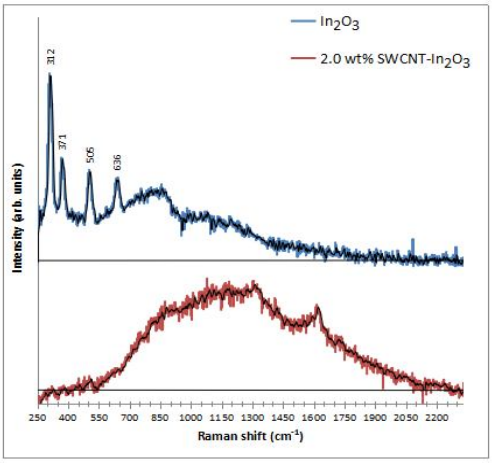



**Figure 3. Raman spectra of $In_2O_3$ and 2.0 wt% SWCNT-$In_2O_3$.**

**B. Ozone-response properties of SWCNT-$In_2O_3$**

The sensing properties of $In_2O_3$, 0.2 wt% SWCNT-$In_2O_3$, 0.5 wt% SWCNT-$In_2O_3$, 1.0 wt% SWCNT-In2O3 and 2.0 wt% SWCNT-In2O3 sensors are studied at room temperature (25℃) under the exposure of 1500 ppb ozone in Table 1. Among the investigated sensing materials, 2.0 wt% SWCNT-$In_2O_3$ sensor exhibits the most excellent ozone-sensing properties (2.0 wt% SWCNT-In2O3 sensor exhibits a response of 13.21, and response and recovery times of 94 s and 92 s, respectively). By contrast, the $In_2O_3$ sensor exhibites a response of 8.92, with response and recovery times of 108 s and 75 s, respectively. As illustrated in Figure 4, the response of 2.0 wt% SWCNT-$In_2O_3$ sensor is increased by the introduction of 1500 ppb ozone and decreased by opening air inlet. In addition, the resistance of 2.0 wt% SWCNT-$In_2O_3$ sensor reaches the original value, and the response and recovery times of 2.0 wt% SWCNT-$In_2O_3$ sensor exhibites no obvious changes after three cycle tests.

| Sensing materials | Response | $t_{90}$/s | $t_{r90}$/s | RH (%) |
|---|---|---|---|---|
| $In_2O_3$ | 8.92 | 108 | 75 | 50 |
| 0.2 wt% SWCNT- $In_2O_3$ | 4.40 | 450 | 349 | 50 |
| 0.5 wt% SWCNT- $In_2O_3$ | 4.15 | 386 | 450 | 50 |
| 1.0 wt% SWCNT- $In_2O_3$ | 6.88 | 107 | 88 | 50 |
| 2.0 wt% SWCNT- $In_2O_3$ | 13.21 | 94 | 92 | 50 |

**Table 1: Sensor responses of 1500 ppbozone gas at room temperature.**

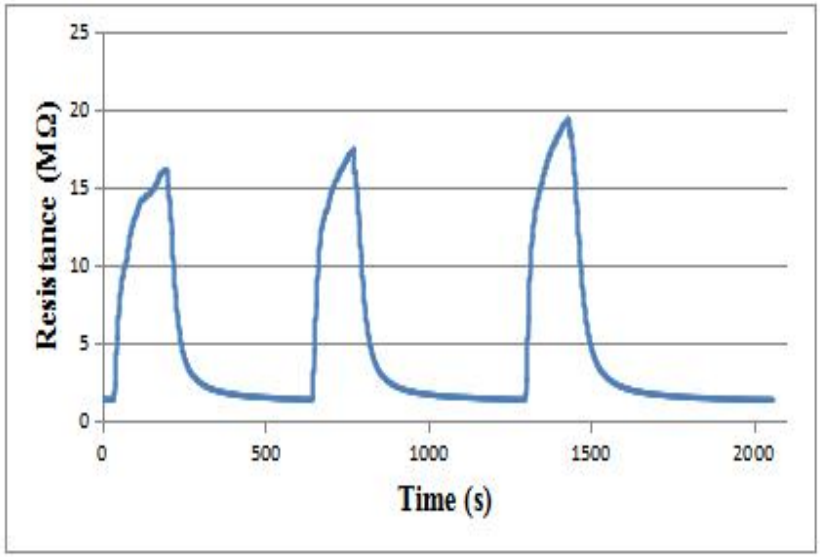



**Figure 4.Resistance signal of the 2.0 wt% SWCNT-$In_2O_3$ to 1500 ppbozone gas at room temperature.**

The 2.0 wt% SWCNT-In2O3 sensor responses are investigated under different ozone concentrations at room temperature, as shown in Figure 5. For all concentrations, the response and recovery times were less than 196 s (Table 2). It can also be found that the 2.0 wt% SWCNT-$In_2O_3$ sensor response increases from 4.41 to 33.11 when the ozone concentration increases from 268 to 2292 ppb. In addition, the responses of the sensor increase nearly linearly with the rising of ozone concentration, indicating that 2.0 wt% SWCNT-$In_2O_3$ sensor exhibits excellent stability for measuring different ozone concentrations.

| Ozone (ppb) | Response | $t_{90}$/S | $tr_{90}$/S | RH (%) |
|---|---|---|---|---|
| 268 | 4.41 | 150 | 192 | 50 |
| 420 | 6.27 | 138 | 196 | 50 |
| 793 | 11.04 | 172 | 174 | 50 |
| 930 | 12.28 | 120 | 168 | 50 |
| 1344 | 16.85 | 144 | 190 | 50 |
| 2165 | 28.80 | 164 | 154 | 50 |
| 2292 | 33.11 | 130 | 150 | 50 |

**Table 2: Sensor response of ozone concentrations from 268 to 2292 ppb on 2.0 wt%SWCNT- $In_2O_3$ at room temperature.**

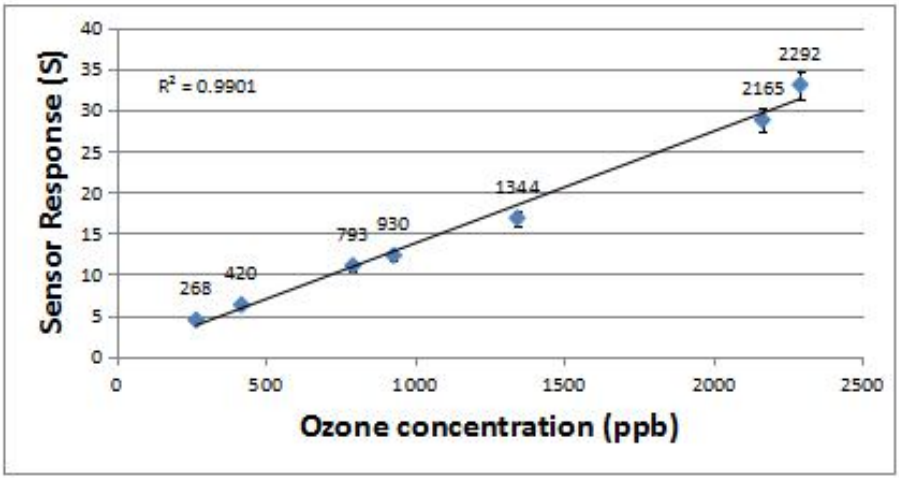



**Figure 5. Response of the 2.0 wt% SWCNT- $In_2O_3$ from 268 to 2292 ppb ozone gas at roomtemperature.**

In order to study the selectivity of the 2.0 wt% SWCNT-In2O3 sensor using various gases including carbon monoxide, hydrogen, ammonia and nitrogen monoxide. The 2.0 wt% SWCNT-In2O3 sensor responses to various gases at 1500 ppb are measured and the results are listed in Table 3. The 2.0 wt% SWCNT-In2O3 sensor exhibites excellent selectivity to ozone at room temperature, which is considerably higher than the sensor to other gases at the same concentrations.

| Various kinds of gases | Concentration (ppm) | Response | $t_{90}$/s | $t_{r90}$/s | RH (%) |
|---|---|---|---|---|---|
| Hydrogen ($H_2$) | 2.5 | 1.00 | --- | --- | 50 |
| Methanol ($CH_3OH$) | 2.5 | 1.53 | 61 | 133 | 50 |
| Ethanol ($C_2H_5OH$) | 2.5 | 1.76 | 37 | 93 | 50 |

| | | | | | |
|---|---|---|---|---|---|
| Nitrogen dioxide ($NO_2$) | 2.5 | 1.11 | 53 | 121 | 50 |
| Carbon dioxide ($CO_2$) | 2.5 | 1.00 | --- | --- | 50 |
| Ozone ($O_3$) | 2.5 | 3.27 | 5 | 24 | 50 |

**Table 3: Sensor response of various gases atroom temperature.**

### C. Probable gas sensing mechanism

The possible ozone sensing mechanism based on SWCNT-In2O3, as presented in Figure 6. The adsorption of ozone on the surface of SWCNT-In2O3. The symbol * represents vacant sites on the surface of the SWCNT-In2O3, as illustrated in Eq.(1). Because ozone is an oxidative molecule, it quickly catches an electron from SWCNT-In2O3. These electrons combined with ozone to form O3– , as shown in Eq.(2). The O3– is decomposed to oxygen molecules and adsorbed O–. Oxygen molecules, which can be desorbed from SWCNT-In2O3. as shown in Eq.(3). The adsorption of O3 involve in the reaction with adsorbed O– as well as released electrons, resulting in a increase in SWCNT-In2O3 resistance (Eq.(4)).

$$(O_3)_{gas} + * \rightarrow O_{3(ads)} \quad (1)$$

$$(O_3)_{ads} + e^- \longrightarrow (O_3)^-_{ads} \quad (2)$$

$$(O_3)^-_{ads} \longrightarrow (O_2)_{gas} + (O^-)_{ads} \quad (3)$$

$$(O^-)_{ads} + (O_3)_{gas} \rightarrow 2(O_2)_{gas} + e^- \quad (4)$$

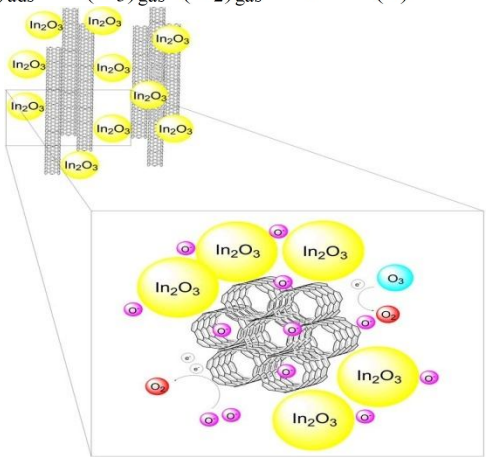



**Figure 6. Scheme of ozone reaction mechanism for the 2.0 wt% SWCNT- $In_2O_3$ sensing material.**

## CONCLUSION

In this study, we have successfully developed a SWCNT-$In_2O_3$ sensor for ozone detection. Among the various ratios of SWCNT-$In_2O_3$, the material 2.0 wt% SWCNT-$In_2O_3$ exhits the highest response (13.21) to 1500 ppb ozone. Furthermore, a possible ozone sensing mechanism of the SWCNT-$In_2O_3$ is presented. The SWCNT-$In_2O_3$ exhibits excellent selectivity for ozone at room temperature. Moreover, the obtained SWCNT-$In_2O_3$ sensor exhibits excellent reversibility, reproducibility and stability, which is a promising sensing material for the detection of ozone.

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