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Single Walled Carbon Nanotube Based Hybrid Nanostructure Gas Sensor Array for Air Quality Index

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Single Walled Carbon Nanotube Based Hybrid Nanostructure Gas Sensor Array for Air Quality Index

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy in

Chemical and Environmental Engineering

by

Heng Chia Su

March 2014

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In the dissertation, the text of chapter 4 is reprinted of the materials as it appears in Nanotechnology 24 (2013) 505502 (11pp), with the co-authors, Miluo Zhang, Wayne Bosze, Jae-Hong Lim and Nosang V Myung.
ABSTRACT OF THE DISSERTATION

Single Walled Carbon Nanotube Based Hybrid Nanostructure Gas Sensor Array for Air Quality Index

by

Heng Chia Su

Doctor of Philosophy, Graduate Program in Chemical and Environmental Engineering
University of California, Riverside, March 2014
Dr. Nosang V. Myung, Chairperson

Chemical sensors have a deep influence in a wide variety of disciplines ranging from biomedical measurement, electrochemical analysis, detection of environmental toxins, pollution monitoring, and warfare threats, to industrial control. The pressure of legislation concerning environmental issues and increasing environmental regulations makes chemical sensing of pollutants extremely important.

The overarching goal of this proposed work is to develop cost effective routes to synthesize integrated 1-D materials onto prefabricated micro-electrodes for the detection of airborne toxins at ambient temperature as well as real-time and simultaneously measuring O₃, CO, SO₂, and NO₂ to quantify Air Quality Index. The sensor arrays will be made out of novel conductometric/chemiresistive sensors based on functionalized single-walled carbon nanotubes (SWNTs). The array will employ sensors with varying sensing materials (organic/inorganic) and sensing mechanisms operated at optimum conditions which will enable more selective and accurate monitoring of AQI. Optimization of both the individual sensor and the sensor array will produce distinctive sensing response patterns
for detecting the individual agents in the gas mixtures. Ink-jet printing will be utilized to deposit hybrid SWNTs inks to precise locations on a substrate, while electrodeposition techniques will be utilized to synthesize metal and metal oxide decorated SWNTs with controlled crystallinity, morphology, and electrical properties. The structure-property relationships of these materials, such as electrical transport, optical and gas sensing performance will be investigated, evaluated, and optimized.
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Figure 5.3 (a) SiO$_2$ chip after 2 minutes O$_2$ plasma (200 W) treatment showed a contact angle of 30°; (b) the same chip after 30 minutes silane treatment showed a contact angle of 17°.
Figure 5.4 Optical images of the electrode after ink jet printing of (a) TS-CuPc and (b) NiPc, respectively. 0.1 mM of individual phthalocyanine solution (TS-CuPc or NiPc) were blended with 0.1 wt% of PEO and 0.026 mg/ml SWNTs, respectively. The substrate temperature was kept at 40 °C during ink jet printing process. The printed ink volume was 0.06 µL.

Figure 5.5 The sensing performance towards SO\(_2\) were correlated with ink jet printing process: (a) SO\(_2\) real-time sensing performance of films printed with 0.015, 0.03, 0.06, and 0.1 µL TS-CuPc solutions (0.1 mM), and (b) the relation of sensing response ($\Delta R/R_0$) and the corresponding printed films resistance.

Figure 5.6 Real-time sensing performances and calibration curves of SWNTs film (blue) and PEO/SWNTs film (orange) towards (a) NO\(_2\) and (b) SO\(_2\), respectively.

Figure 5.7 (a) I-V curves of the TS-CuPc, NiPc, FeOEP, FeTPP, NiTPP, and RuTPP ink jet printed films, respectively, and (b) their electron transfer characteristics [Current (I_SD) vs. back gated voltage (V_G)].

Figure 5.8 Real-time sensing performances and calibration curves of ink jet printed films towards (a) NO\(_2\), (b) SO\(_2\), and (c) O\(_3\) in the absence of light, respectively.

Figure 5.9 Real-time sensing performances and calibration curves of ink jet printed films towards NO\(_2\) (a) under red light illumination, (b) under green light illumination, and (c) under UV light illumination, respectively.

Figure 5.10 Real-time sensing performances and calibration curves of ink jet printed films towards SO\(_2\) (a) under red light illumination, (b) under green light illumination, and (c) under UV light illumination, respectively.

Figure 5.11 Real-time sensing performances and calibration curves of ink jet printed films towards O\(_3\) (a) under red light illumination, (b) under green light illumination, and (c) under UV light illumination, respectively.

Figure 5.12 Sensitivity of Ink-jet printed film of Ts-CuPc/SWNTs hybrid nanostructures (red), and NiPc/SWNTs hybrid nanostructures (green), FeOEP/SWNTs hybrid nanostructures (blue), and FeTPP/SWNTs hybrid nanostructures (magenta), and NiTPP/SWNTs hybrid nanostructures (magenta), and NiTPP/SWNTs hybrid nanostructures (orange), and RuTPP/SWNTs hybrid nanostructures (pink) as well as SnO\(_2\)/SWNTs hybrid nanostructures (grey), and Pt/SnO\(_2\)/SWNTs hybrid nanostructures (dark yellow) towards NO\(_2\), SO\(_2\), CO, and O\(_3\).
1 INTRODUCTION

1.1 Air Quality Index

Human health is closely related to air pollution levels from the environment in daily life. Ill-health endpoints such as pulmonary impairment associated with exposure to common pollutants, increased the risks of asthma attacks and respiratory/cardiovascular disease. Poor air quality conditions including acid rain formation and particulate matter formation increased daily mortality\textsuperscript{1}. Numerous studies have revealed that a lot of health issues may be attributed to short or long-term exposure and to different exposure-response characteristics\textsuperscript{1,2}. Owing to the serious air pollutions in the urban area and the related health issues, the development of an adequate tool to understand pollution levels in an area is of extreme importance\textsuperscript{2}. In order to confront air pollution problems and to plan the strategies to diminish the air pollution, both the scientific community and the relevant authorities have focused on monitoring and analyzing the atmospheric pollutants concentration. Under the numerous efforts of related authorities, Pollution Standers Index (PSI) was established in 1976. Afterwards, in order to provide accurate, up to date and comprehensible advices concerning the daily levels of atmospheric pollution in terms of health protection, the US Environmental Protection Agency (EPA) developed Air Quality Index (AQI) based on five pollutants, namely O\textsubscript{3}, NO\textsubscript{2}, CO, SO\textsubscript{2} and PM\textsubscript{10}, based on the Clean Air Act\textsuperscript{2}. The AQI provide information about outdoor air quality as easy to find and understand as a weather forecast.\textsuperscript{3} As shown in Table 1, the AQI includes both a quantitative measurement of air quality and guidance about potential health effects of pollution. Basically, AQI provide a
convenient way to tell how clean the air is, and what associated healthy effects might be a concern for public. The AQI runs from 0 to 500. A higher AQI value indicates a greater level of air pollution and a greater health concern. An AQI value of 100 generally corresponds to the national air quality standard for the pollutant, which is the level EPA has set to protect public health\(^4\).

Table 1.1 Air Quality Index levels of health concern

<table>
<thead>
<tr>
<th>Air Quality Index Levels of Health Concern</th>
<th>Numerical Value</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good</td>
<td>0 to 50</td>
<td>Air quality is considered satisfactory, and air pollution poses little or no risk</td>
</tr>
<tr>
<td>Moderate</td>
<td>51 to 100</td>
<td>Air quality is acceptable, however, for some pollutants there may be a moderate health concern for a very small number of people who are unusually sensitive to air pollution.</td>
</tr>
<tr>
<td>Unhealthy for Sensitive Groups</td>
<td>101 to 150</td>
<td>Members of sensitive groups may experience health effects. The general public is not likely to be affected.</td>
</tr>
<tr>
<td>Unhealthy</td>
<td>151 to 200</td>
<td>Everyone may begin to experience health effects; members of sensitive groups may experience more serious health effects.</td>
</tr>
<tr>
<td>Very Unhealthy</td>
<td>201 to 300</td>
<td>Health alert: everyone may experience more serious health effects.</td>
</tr>
<tr>
<td>Hazardous</td>
<td>301 to 500</td>
<td>Health warnings of emergency conditions. The entire population is more likely to be affected.</td>
</tr>
</tbody>
</table>

AQI is calculated by the following equation\(^2\):

\[
I_p = \frac{I_{HI} - I_{Lo}}{BP_{HI} - BP_{Lo}} (C_p - BP_{Lo}) + I_{Lo}
\]  

(1)

Where

\(I_p\): The index for pollutant p

\(C_p\): The rounded concentration of pollutant p
$BP_{Hi}$: The breakpoint that is greater than or equal to $C_p$

$BP_{Lo}$: The breakpoint that is less than or equal to $C_p$

$I_{Hi}$: The Air Quality Index value corresponding to $BP_{Hi}$

$I_{Lo}$: The Air Quality Index value corresponding to $BP_{Lo}$

Table 2 give the detail health, the categories for AQI, the range of index values and pollutant concentrations for each category from the EPA website.

**Table 1.2 Break point for the AQI for each pollutant**

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>PM$_10$ (µg/m$^3$)</th>
<th>PM$_{2.5}$ (µg/m$^3$)</th>
<th>CO (ppm)</th>
<th>SO$_2$ (ppm)</th>
<th>NO$_2$ (ppm)</th>
<th>AQI</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_3$ 8-hour</td>
<td>-</td>
<td>0.0-54</td>
<td>0.0-15.4</td>
<td>0.0-4.4</td>
<td>0.000-0.035</td>
<td>0.000-0.053</td>
</tr>
<tr>
<td>O$_3$ 1-hour</td>
<td>-</td>
<td>55-154</td>
<td>15.5-40.4</td>
<td>4.5-9.4</td>
<td>0.036-0.075</td>
<td>0.54-0.1</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>0.076-0.095</td>
<td>0.125-0.164</td>
<td>155-254</td>
<td>40.5-65.4</td>
<td>9.5-12.4</td>
<td>0.076-0.185</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>0.096-0.115</td>
<td>0.165-0.204</td>
<td>255-354</td>
<td>65.5-150.4</td>
<td>12.5-15.4</td>
<td>0.186-0.304</td>
</tr>
<tr>
<td>CO</td>
<td>0.116-0.374</td>
<td>0.205-0.404</td>
<td>355-424</td>
<td>150.5-254.4</td>
<td>15.5-30.4</td>
<td>0.305-0.604</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>0.405-0.504</td>
<td>0.425-0.504</td>
<td>250.5-350.4</td>
<td>30.5-40.4</td>
<td>0.605-0.804</td>
<td>1.25-1.649</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>0.505-0.604</td>
<td>0.505-0.604</td>
<td>350.5-500.4</td>
<td>40.5-50.4</td>
<td>0.805-1.004</td>
<td>1.65-2.049</td>
</tr>
<tr>
<td>NA</td>
<td>0.605 or above</td>
<td>0.605 or above</td>
<td>500.5 or above</td>
<td>50.5 or above</td>
<td>1 or above</td>
<td>2.05 or above</td>
</tr>
</tbody>
</table>

The current analytical tools available for AQI monitoring have some significant limitations. There is a great need of new instruments that (1) can respond rapidly, even
instantly, towards the changes in the analytes concentrations, (2) can simultaneously detect a wide spectrum of analytes, (3) have high sensitivity at ultra-trace levels with reproducibility, (4) have high selectivity to specific analytes, (5) require little or no sample preparation, (6) consume minimal amounts of reagents, and (7) are simple, consume little power, and are portable for in-field operations. Miniaturized and automated analytical instruments, suitable for real-time measurements, are preferred since they enable fast warning, effective protection of personnel, and informed decision making.

1.2 Gas Sensors: An Overview

The ability to monitor contaminants in a specified environment has always been important not only to ensure the health and safety of people, but it is essential to maintain equipment integrity. The electronic nose, or E-nose, that was initially used for quality control in the food, beverage and cosmetics industries, is now being advanced as a promising device to accurately identify, differentiate, and quantify the presence of hazardous gaseous chemicals \(^5\). These advanced applications range from the detection of pollutants and gas leaks for environmental protection at the parts per billion levels, to the detection of odors specific to diseases approaching the parts per trillion levels. E-nose system which simulated the human olfactory was advanced as a promising device to accurately identify, differentiate, and quantify the presence of hazardous gaseous chemicals to improve the quality of lives\(^5\).

A chemical sensor is a device that interacts with gaseous chemical compounds and then changes its electrical property in terms of resistance, or current, to output signals that can be quantified directly or indirectly. Figure 1.1 illustrates the essential elements of a gas
sensor. Basically, it consists of two important parts: a sensitive layer and a transducer. The Sensitive layer is responsible for recognizing the analyte gas while the transducer will transfer the property change of the sensing element to a measurable signal.

Odors or toxic chemical gaseous compounds

**Figure 1.1** Schematic representation of a gas sensor with a sensitive layer and a transducer.

Over the years, several sensor configurations have been developed by detecting different changes of transducers properties ranging from piezoelectric sensors\(^6\) (which monitor the frequency change of polymers functionalized/coated electrodes when absorb gaseous molecules) to chemiresistive/conductometric sensors\(^7\) (which generate the electrical resistance/conductance change upon gas adsorption/reaction on semiconducting sensing materials), Figure 1.2(a).
Figure 1.2 Schematic representations of the (a) configuration of the different type of gas sensor and (b) a typical response curve for a chemiresistive gas sensor.

Among the different configurations, the gas sensor based on electronic properties change remains of extensive and intense interests for its simplicity for operation. The operation is based on measuring the change in the resistance change of the sensing element when expose to analyte. The response curve in Figure 1.2(b) is typically characterized by the following parameters:

1. **Sensitivity (S):** The change in measurement signal per concentration of the analyte.

2. **Selectivity:** The ability to discriminate or preferentially respond to specific analyte.
3. **Response time**: The time required for a gas sensor to respond. It is a time interval that signal reaches to a fixed percentage change (usually 90%) of the final value when exposed to analyte.

4. **Recover time**: The time interval required for a sensor to return to its 90% of the original state.

5. **Lower detection limit (LDL)**: The minimum concentration that causes a signal three times higher than the sensor’s intrinsic signal.

6. **Upper detection limit (UDL)**: The maximum concentration of an analyte gas that can be reliably detected by the sensor.

7. **Dynamic range**: The concentration range between the lowest possible detection limit to the upper limit concentration.

Compared to other sensor modes, chemiresistive metal oxide sensors drew researchers’ attention because of the robust nature, simple circuit design, low-cost for miniaturized and in-field deployable operation. Despite of great sensitivity, fast response/recovery time, and long life time, metal oxide based chemiresistors need to operate at high temperature which ultimately increased the power consumption. The conducting polymers based chemiresistors have advantages of room temperature operation, good response to a wide range of analytes, fast response/recovery time to polar gaseous compounds, but disadvantages of short life time, resistance drift, and huge interference from humidity. Consequently, facile approaches, which provide considerable benefits in terms of low cost and manufacturability for mass production, to generate rapid response, reversible and
selective gaseous chemical detection sensor array at room temperature, are essential for environmental monitoring.

1.3 Gas Sensors Based on Nanostructure Materials

With recent advances in nanotechnology and Nano/Micro Electromechanical Systems (NEMS/MEMS), it is now feasible to construct chemiresistive/conductometric sensors using one-dimensional (1-D) nanostructures, such as nanowires, nanobelts, nanosprings, and carbon nanotubes (CNTs). Such structures are attractive for nanosensors because they offer significant advantages over other materials. First, they can be functional both as sensing elements and as the transducers. Second, the diameters of these nanostructures are comparable to those of analytes being sensed. After analytes bind to the surface of 1-D nanostructures it can lead to depletion or accumulation of carriers in the ‘bulk’ of the nanometer diameter structure versus only the surface region of a planar device, giving rise to large resistance/conductance changes to the point that single-molecule detection is possible\(^8\) (Figure 1.3). Third, since the devices directly convert chemical information into an electronic signal, existing low powered microelectronic technology to be used for creating miniaturized sensor systems. Finally, the small size of nanostructures makes possible the development of high density arrays of individually addressable nanostructures for simultaneous analysis of a range of different species and passive redundancy to reduce false positives/negatives. Various 1-D nanostructures with different functional surface properties, composition and morphologies have been fabricated by utilizing both bottom-up and top down fabrication routes for gas sensing application\(^9\).

The summary below is primarily limited to 1-D nanostructures such as nanowires,
nanobetsls, and nanotubes with the electronic properties are significantly influenced on gas sensing.

**Figure 1.3** Schematic representation of the Debye length (surface depletion layer) within nanostructures upon adsorption of the analyte.

### 1.3.1 Single Walled Carbon Nanotube Gas Sensors

Single walled carbon nanotubes (SWNTs) are a promising 1-D nanomaterial due to their excellent electronic properties, and thermal and chemical stability under room temperature to develop devices with miniaturized size, simplicity, reliability, and low cost. The unique properties of SWNTs have motivated researchers to advance on the SWNTs based chemical sensors. Among them, SWNTs based chemiresistor has been widely applied due to their sensitivity toward various gaseous analytes via charge interaction and simple measurement set up. Pristine SWNTs shows remarkable adsorptive ability due to large surface area and once interact with NH$_3$, NO$_2$ and aromatic compounds, the electric behavior change depending on the exposing analytes; nevertheless, as a sensing material, pristine SWNTs have drawbacks specifically on low sensitivity, lack of selectivity and long recovery which hinder its use to make an applicable gas sensor. Numerous efforts have been devoted to surface functionalization of SWNTs, covalently or
noncovalently, to improve their sensing performances including sensitivity and selectivity\textsuperscript{14}. Current progresses have shown that sensitivity towards certain analytes can be further enhanced by introducing functional groups\textsuperscript{15,16}. Numerous synthetic routes have been reported for the preparation of functionalized SWNTs; each provided controlled size and distribution of the decorated SWNTs to some extent. These approaches can be divided into three general categories: 1) electrochemical and chemical processes\textsuperscript{17,18}, 2) dispersion of nanoparticles on the surface of SWNTs \textsuperscript{19}, and 3) physical deposition including sputtering and e-beam evaporation\textsuperscript{20}. Although a large variety of the metal nanoparticles decorated carbon nanotubes have been successfully synthesized via physical routes, expensive equipment and high power consumption are the major concern and disadvantages. Homogeneous, highly stable and highly concentrated dispersed SWNTs with similar particle size distributions could be achieved from dispersion of nanoparticles. However, special functionalization steps of SWNTs are needed, e.g., chemically functionalized SWNTs with thiol group (–SH)\textsuperscript{19} to react with gold. Moreover, extra purification steps are needed, which resulted lower yield for the final SWNTs.

Although SWNTs with various functional groups, such as carboxylic and PABS groups can help to enhance the solubility of SWNTs in solution, they also induce defects that destroyed the intrinsic structurals, mechanical and electrical properties of the SWNTs\textsuperscript{21}. In order to maintain the nanotubes intrinsic properties, noncovalently bonded surfactants were introduced to separate the carbon nanotubes into smaller bundles or individual tubes. Pristine SWNTs have been successfully dispersed in aqueous media by the asisstant of sodium dodecyl sulfate (SDS)\textsuperscript{22}, sodium cholate\textsuperscript{23}, sodium dodecylbenzene sulfonate
(SDBS)\textsuperscript{24}, and polymer rapping\textsuperscript{25}. In particular, Deoxyribonucleic acid (DNA) was found to have better dispersion efficiency than other polymers\textsuperscript{26}. This is attributed to the $\pi$-stacking interaction which overcomes the van der Waals attraction energy of 500 ev/µm\textsuperscript{27} that exists between each carbon nanotube\textsuperscript{28}. Current progress in SWNTs has shown that sensitivity towards certain analytes can be further enhanced by introducing functional groups\textsuperscript{14}. Metal or metal oxide decorated SWNTs by means of electrochemical deposition have demonstrated the capability to enhance both selectivity and sensitivity towards specific target analytes, including Pd for H$_2$\textsuperscript{18}, Au for H$_2$S\textsuperscript{29}, and ZnO for H$_2$S\textsuperscript{30} and VOCs\textsuperscript{14}. Furthermore, instead of decorating SWNTs with inorganic compounds, functionalizing the surface of SWNTs by chemically or electrochemical techniques with conducting polymers; e.g. PEDOT-PSS or polyaniline (PANI), and polythiophene\textsuperscript{31,32} has shown great sensing performance.

### 1.3.2 Metal Oxide Based Gas Sensors

Metal oxides have been reported as good sensing materials for various analytes\textsuperscript{33}. In particular, semiconducting metal oxides such as ZnO\textsuperscript{34}, SnO$_2$\textsuperscript{35-37}, MoO$_3$\textsuperscript{38}, In$_2$O$_3$\textsuperscript{39} and Ga$_2$O$_3$\textsuperscript{36,40} were reported as good candidates for sensing gases such as CO, NO$_2$ and NH$_3$ under elevated temperature. In fact, most commercialized solid state gas sensors are based on metal oxide (mainly SnO$_2$ or ZnO). The principle of metal oxide sensing mechanism depends on the surface reactions with the gas species.

Among those metal oxides, SnO$_2$ is commonly used to detect CO owing to its excellent surface catalytic oxidation of CO\textsuperscript{41}. At elevated temperature, oxygen vacancies
are created on the oxide surface due to the chemisorption of molecular oxygen\textsuperscript{42,43}. In Figure 1.4, the schematic representation showed partial reduced SnO\textsubscript{2} surface with oxygen vacancies which chemisorb molecular oxygen. This molecular adsorption can build up negative charges on the metal oxide surface as well as create a space charge layer. Reducing gases, such as CO and H\textsubscript{2}, donate (release) (Figure 1.4) electrons to the metal oxide which increase the conductivity, while oxidizing gases, such as NO\textsubscript{2} and O\textsubscript{2}, extract electrons from the space charge layer region and create chemical bonding on the metal oxide surface which decreases the conductivity\textsuperscript{43}.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Schematic representation of partially reduced (110) SnO\textsubscript{2} surface with and the surface adsorbed molecular oxygen species.}
\end{figure}

SnO\textsubscript{2} is a n-type semiconductor with a wide band gap of ~ 3.6eV. The excellent chemical stability, and sensing capability which makes it a suitable transducer material in gas sensors\textsuperscript{36}, solar cell\textsuperscript{44}, optical device\textsuperscript{45}, and component in Li ion battery\textsuperscript{46}. However, due to its high resistivity at ambient temperature as synthesized, SnO\textsubscript{2} as a transducer element must be operated at an elevated temperature for optimal performance\textsuperscript{35,47}. To overcome this, 1-D nanomaterials such as SWNTs are being utilized to synthesize hybrid
structures for room temperature gas sensing applications\textsuperscript{48-50}. Various methods including electrospinning\textsuperscript{51}, thermal evaporation\textsuperscript{20}, and hydrothermal synthesis\textsuperscript{52} have been developed, however, their hybrid nanostructures either lack of thickness control or are in need of expensive equipments.

1.3.3 Porphyrin and Phthalocyanine Based Gas Sensors

Porphyrin (Por) [Figure 1.5(a)] is an organic macrocyclic compound consisting of four pyrrole molecules linked together by four methane bridges\textsuperscript{53}. These compounds are large delocalized $\pi$ aromatic systems having flat and planar structures. The resultant compound has unique structural and optical properties, and are chemical stable\textsuperscript{54}. They are able to bind nonspecifically with different analytes through van der Waal forces, hydrogen bonding, electrostatics and coordination interactions with the central metal ion\textsuperscript{55}. The presence of four nitrogen atoms in the center of the macrocycle makes them the most versatile chelating system and hence they can coordinate with metals to form metalloporpyrins. For decades, porphyrins and metalloporphyrins have been the topics of numerous studies. This is because of the fact that certain porphyrin derivatives, such as meso-tetraphenylporphyrin (TPP) [Figure 1.5(b)] and octaethylporphyrin (OEP) [Figure 1.5(c)], play a key role in different essential biological processes such as photosynthesis, dioxygen transport and storage, and electron transfer\textsuperscript{55}. Apart from the metal coordination interaction with gas analytes, the abundance of a wide range of synthetic porphyrins having different peripheral subunits and central metal atoms makes the porphyrins a potential building block for the development of chemical sensors or sensor arrays\textsuperscript{55}. The sensing
capabilities of porphyrin thin films have been demonstrated based on optical\textsuperscript{56}, mass detection\textsuperscript{55}, and thin-film-based field effect transistor (FET)\textsuperscript{57-59}.  

**Figure 1.5** Schematic representation of the molecular structure of (a) porphyrin, (b) meso-tetraphenylporphyrin and (c) octaethylporphyrin.

Phthalocyanines (Pc) [Figure 1.6(a)] are analogues of porphyrins. Phthalocyanines have been widely used in the area of dyes and pigments, active components in dye-sensitized solar cells\textsuperscript{60,61}, medical imaging and photodynamic therapy, and especially as gas sensors\textsuperscript{62-65}. In particular, Metal Phthalocyanine (MPc) [Figure 1.6(b)] gains numerous attention as a component in gas sensor applications especially for NO\textsubscript{2}, SO\textsubscript{2}, and O\textsubscript{3}\textsuperscript{62}. The selectivity and sensitivity of phthalocyanine can be tuned by changing the central metal ion and the substituent groups around the periphery of the molecule\textsuperscript{62}. Thin films and crystals are conveniently prepared by the Langmuir-Blodgett (LB) technique, spin coating or by thermal evaporation\textsuperscript{62}. When the resultant film or single crystal\textsuperscript{63} is exposed to an oxidizing or reducing gas, its conductivity changes accordingly. For example, when the electron withdrawing NO\textsubscript{2} chemisorb onto MPc, surface charge-transfer interactions occur, which
means electrons flow from MPc to NO$_2$ and more holes are formed in MPc. Since the main charge carriers for the p-type semiconducting phthalocyanines are holes, the charge transfer then increases the conductivity$^{65}$. The change of the conductivity forms the basis of a simple sensor. However, the currents measured from the device are very low (e.g. nanoamperes) leading to small signal-to-noise ratios and increasing the difficulty of measurement.

![Schematic representation of the molecular structure of (a) metal-free phthalocyanine and (b) metal phthalocyanine.](image)

**Figure 1.6** Schematic representation of the molecular structure of (a) metal-free phthalocyanine and (b) metal phthalocyanine.

### 1.4 Delivery and Alignment of Nano-engineered Materials

Achievements of the nanotechnology provide a novel route to manipulate the deposition pathway of 1-D nanomaterials. Conventional deposition processes for nanomaterials include chemical vapor deposition (CVD), alternating current (ac-) dielectrophoresis and photolithography, which provide different routes to assemble the nanomaterials onto electrodes to fabricate devices. Although CVD process can deposit materials in bulk, high operating temperature limits the access to deposit organic materials. While Ac-dielectrophoresis is widely used for simultaneous and site selective deposition of 1-D nanomaterials$^{66}$, lack of scalability for bulk fabrication make it hard to be amenable
for wafer level fabrication. Alternatively, photolithography provides precisely patterning on wafer scale fabrication and micro scale feature (~ 3 micron), but the expensive cost and time consuming in clean room processes limit the practical application of this technique.

Printing technology was proposed to deliver the nanomaterials such as conducting polymer with high reproducibility and scalability, and low cost. In general, printing is a reproduction process in which ink is applied to a substrate in order to transmit the images or messages. Typical printing process can be divided into two categories depending on whether a printing plate is needed or not. Among the printing technologies available, screen printing and ink jet printing are the most commonly used in production and fabrication. Screen printing is a process in which ink is forced through a screen to form patterns. The printing plate is a combination of stencil and screen that provides the patterns. In order to obtain the fine feature, the screen printable ink must have high viscosity under no sheer from the squeegee, but thinning when being forced through the screen allowing ink pass through the stencil to the substrate. Upon the sheer force eliminates, it recovers to viscous state forming a sharp image with well-defined boundaries. Typical thickness of the screen printed patterns is about 20-100 microns determined by the stencil and dimension of the mesh; therefore, screen printing process falls into the category as thick film technology, the width of whose pattern is around 100 microns. Although the screen printing process is suitable for large area printing and bulk fabrication, it is hard to produce the miniaturized pattern for high density sensor arrays.

Ink jet printing is the most promising method for the deposition of functional materials on the selected area. In general, ink jet printing technology can be categorized
as continuous printing and drop on demand. Continuous ink jet technology generates a constant stream of ink droplet, and drop on demand produces a droplet only if it is required by the image. There are two kind of drop on demand processes; one is thermal ink jet and the other one is piezoelectric ink jet process. Thermal ink jet generates droplets by the pulse of current passing through the heating element and locally vaporizes ink in the jetting chamber. However, due to the construction of the jetting mechanism only water could be the solvent due to the vapor point. This limits the printing of the materials that only dissolve in organic solvent. With piezoelectric drop on demand ink jet process, a droplet is formed and jet out by mechanically deforming the piezoelectric material in the chamber. An electronic signal wave form of the jetting process is controlled by the preprogrammed software that determined by the properties of the solvent. Therefore, inks based on either organic or aqueous solvents are suitable for piezoelectric ink jet printer. The reason ink jet printing technology is of interest for the application of high resolution manufacturing owing to attractive features include (1) ability of purely additive on top of the existing features or patterns where are needed, (2) flexibility of choosing structure design by simplify changing the software based on printer control system, (3) ability to pattern the organic materials such as biological materials (DNA/RNA or proteins) that are not compatible with conventional photolithography alignment process, (4) compatibility for bulk/wafer scale printing with high repeatability, and (5) low cost.

Since ink droplet would be affected by the viscosity and surface tension of the ink, jetting speed, particle size in the solvent, substrate conditions, environment humanity and temperature, jetting conditions should be carefully tuned to generate homogeneous and
correctly directed ink droplet in order to obtain the uniform printed pattern. However, challenges in the development of ink jet printing technology are arising not only from making appropriate inks that provide compact homogenous feature with fine resolution and conductivity, but also from the unwanted and inhomogeneous drying of liquid droplets on the flat substrate which is known as coffee ring effect. This kind of ring like stains are not particular to coffee but are a general phenomenon which can be seen in daily life such as the residue on glassware. In general, this is because of the solute is not uniformly distributed in the liquid prior to dry. The coffee ring effect has been explained by Deegan et al. as a result of the uneven evaporation of a liquid over a droplet’s liquid – air interface at the droplet’s edges which subsequently generates an internal flow that compensates the material loss due to evaporation. Therefore, a continuous replenishing flow carries the solutes as close as possible to the boundary of a droplet and deposit upon evaporation of the solvent. Moreover, the same research group also found that gravitational effect, electric field, and temperature gradients did not play an essential role. When the drop was locally heated up, circulating flow appeared, but the ring deposition was not changed.

Significant amount of the researches on minimizing or eliminating coffee ring effect have been conducted. The most common approaches are by increasing the substrate temperature, which stimulates evaporation rate of solvent, or by using a combination of two solvents with different boiling temperature, which compensate the high evaporation rate around the droplet’s edge. The purpose of elevating the substrate temperature is to reduce the internal compensate flow to carry the solute into the droplet edge; however, there are two potential problems arise from increasing substrate temperature. First, heat
accelerates the solvent evaporation rate; therefore, the hot air between inkjet head and substrate would rapidly evaporate droplet in the air during printing. Second, multiple rims form within the droplet at higher (~60°C) substrate temperature creating the discrete circle pattern. The other method to mix two solvents with different boiling temperature is not suitable in this study, because the usage of DNA that will precipice out in the presence of alcohol. Other than the two approaches mentioned above, surface treatment of the substrate is the another route to create homogenous distribution of the solute. In order to create hydrophilic surface, oxygen plasma has been used \textsuperscript{16}. Hydrophilic surface can reduce the contact angle of droplet resulting in the better distribution of solute and minimize the coffee ring effect.
1.5 Electrodeposition for site specific deposition

In recent year, a variety of novel techniques have been proposed for synthesis of nanostructures and fabrication of functional nanoengineered devices including chemical and biological sensors, photovoltaics, and nanoelectronics, etc. Among those techniques, electrodeposition has several advantages including (1) simplicity, (2) ambient operation conditions, (3) ability to tailor the materials properties such as grain size, composition and crystal orientation, (4) capability to deposit various materials including metals, metal oxides, and conducting polymers and (5) site specific deposition. Table 3 summaries the comparison of the conventional deposition processes.

**Table 1.3** Comparison of Conventional Processes to Fabricate Hybrid nanostructures

<table>
<thead>
<tr>
<th>Deposition Method</th>
<th>Electrochemical</th>
<th>Chemical</th>
<th>Physical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Electrodeposition, and Electroless deposition</td>
<td>Hydrothermal, Solvothermal, Chemical precipitation</td>
<td>Spin coating, Sputtering, E-beam or Thermal evaporation, and Ion irradiation</td>
</tr>
<tr>
<td>Cost</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Scalability</td>
<td>√</td>
<td></td>
<td></td>
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<tr>
<td>High Throughput</td>
<td>√</td>
<td>√</td>
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<tr>
<td>Site Specific Deposition</td>
<td>√</td>
<td></td>
<td></td>
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<tr>
<td>Uniform Particle Size Distribution</td>
<td>√</td>
<td>√</td>
<td>√</td>
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<tr>
<td>Capability to Deposit Varies Materials</td>
<td>√</td>
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</tbody>
</table>
Electrodeposition is a process that a potential difference is applied to electrodes at an electrolyte interface resulting in the electron transfer between the electrode and an ionic species in the electrolyte. The ionic species are subsequently deposited onto the electrodes. The electrodeposition has been utilized to fabricate nanostructures such as nanowires\textsuperscript{72,73}, nanotubes\textsuperscript{74}, and nanoparticles\textsuperscript{75}.

The mechanism of electrodeposition can be explained in details as follows. First, potential applied between two electrodes serves as electrochemical driving force for the electrolyte cation reduction at the electrode surface. Second, as the electron inject from the electrode into the cation, the cation is reduced into an adatom and migrates over the electrode surface to an energetically favorable site. Third, further reduction and aggregation of adatoms results the formation of nuclei. Finally, the nuclei aggregate and lead to the growth and coalescence of nanoparticles\textsuperscript{76}. The energetically favorable sites include scratches, dislocation, steps, kinks, and other defects\textsuperscript{76}. Take SWNTs as example, the side wall of SWNTs contain the defect sites such as Stone-Wales defects\textsuperscript{77} (pentagon-heptagon pairs), sp\textsuperscript{3}-hybridized defects, and vacancies in the nanotube lattice\textsuperscript{78}. The defect sites serve not only the active center for electrochemical functionalization but also the active sites for catalytically reactions.

1.6 Objective of the Thesis and Organization

1.6.1 Research Objectives

The need of chemical detection and quantification is an increasingly important demand in our daily lives. It is urgent to develop the means to monitor the environment for
pollutants or toxins, ensure homeland security, maintain operation and emission control in the industrial and automobile sectors, and diagnose health problems. Nanosensors, in particular, have gained attention because its better performance, lower cost, and compact and highly deployable designs. Among the different sensing modalities, electrical sensing, SWNTs based chemiresistive gas sensor in this work, have demonstrated some of the most drastic gains due to the augmented effect of catalytic and adsorption processes on charge carrier behavior. This includes reducing energy consumption and operating temperature requirements while dramatically increasing sensitivity and reducing response/recovery time. The diminutive sizes of nanosensor elements are also conducive to smart sensor platforms that exploit massive parallelism to distinguish multiple analytes and their concentrations in complex mixtures.

The overarching goal of the proposed work is to develop cost-effective nanomanufacturing processes to synthesize nanoengineered materials with “tailored-made” properties and to assemble and integrate these materials to high density micro-fabricated sensor arrays to detect and quantify AQI in real-time by simultaneously measuring O₃, CO, SO₂, and NO₂. The specific aims of this work were as followings:

1) Develop cost effective techniques to functionalize SWNTs and understanding fundamental issues regarding functionalization/modification of SWNTs with different materials.

2) Develop SWNTs based hetero-nanostructure with controlled crystallinity, morphology, and electrical properties for airborne toxins monitoring.
3) Investigate the light and environmental temperature effect on the selectivity and sensitivity towards specific gas.

4) Demonstrate the capability to fabricate high density individual addressable gas sensor arrays using functionalized SWNTs for simultaneous detection of multi-analytes.

1.7 Thesis Organization

This thesis is organized as follows. In chapter 2, a brief introduction on electrochemical functionalization of SWNTs is provided, followed by description of the fabrication of SnO$_2$ decorated SWNTs. The real time gas sensing response towards CO, NO$_2$, and NH$_3$ in the absence of light was optimized by controlling the deposition potential, deposition charge density and the annealing temperature. The selectivity and sensitivity under UV light illumination was also investigated and presented.

In chapter 3, sequential functionalization of SnO$_2$/SWNTs hybrid nanostructures with Pt for CO sensing is optimized. The surface morphology, growth mechanism and room temperature sensing performance as well as the effect of light illumination and environmental temperature were investigated.

Chapter 4 described the development of SWNT-based hybrid nanostructures sensor array via electrochemical reduction and ink jet printing process to detect airborne toxins. DNA is utilized to work as dispersion agent for soluble SWNTs as well as metal ions chelation/nucleation sites. High density sensor arrays are achieved through ink jet printing positioning process followed by electroless deposition. The sensing performance towards
aribone toxins (i.e., H₂, H₂S, NO₂, and NH₃) is quantified by tailoring the type of deposited metals and the size of the metal nanoparticles with different metal ion precursors and various concentrations. Selectivity and sensitivity towards targeted different analytes is characterized and optimized.

Chapter 5 deals with the porphyrin and phthalocyanine based SWNTs gas sensor arrays via ink jet printing process for AQI monitoring. The sensing pattern was established by creating high density sensor arrays with various metalloporphyrins and metallophthalocyanine. Their sensing performances towards O₃, CO, SO₂, and NO₂ without light and under the illumination of different wavelength LED lights are systematically investigated.
1.8 References


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2 Tin Dioxide Functionalized Single Walled Carbon Nanotubes
Hybrid Nanostructure for Environmental Monitoring

Abstract:
Hybrid nanostructures of functionalized SWNTs decorated with tin dioxide, SnO$_2$, were synthesized on prefabricated microelectrodes by an electrochemical process. The SnO$_2$ provides active surface sites of O$^-$ and O$_2^-$ that analyte gases react with by either transferring electrons to or removing them from the SWNTs causing positive or negative changes in the nanostructure’s resistance in accordance with the chemical nature of the gas and in proportion to their concentration in the environment. The sensitivity and selectivity of the SnO$_2$/SWNTs hybrid gas sensors were studied as a function of electrochemical fabrication conditions including deposition potential, charge density, and subsequent calcining temperature towards CO, NO$_2$, and NH$_3$, respectively, and under both ambient conditions and UV illumination. The sensitivity of the CO, NH$_3$, and NO$_2$ in the absence of the light was 0.31, 5.5, and 12.4 %/ppm, respectively, with each optimum fabrication condition. In the presence of light, the sensitivity of CO increased to 0.86 %/ppm with lower detection limit of 0.5 ppmv. This study illustrates the great potential of nanotechnology providing functional nano-systems based on nanoelectronic hybrid nanostructures for highly sensitive room temperature gas sensing applications.
2.1 Introduction

Chemical sensing based on various nanostructures\(^1\) has attracted enormous attention—where gas sensing is now widely held as one of the most promising areas where nanotechnology will have a significant impact. Advancements in nanotechnology have prompted the utilization of one-dimensional (1-D) semiconducting nanostructures as novel transducer materials\(^2\) in sensing devices due to their ultra-high surface area- to- volume ratio that enhances surface adsorptive capacity, tunable electrical properties via dopants, and the ability to form ultra-high density arrays in small dimensions. In particular, single walled carbon nanotubes (SWNTs) have become a promising 1-D nanomaterial to develop devices with miniaturized size, simplicity, reliability, and low cost\(^3\)-\(^5\). Even though pristine SWNTs display very poor sensitivity and selectivity as a gas sensing material, its unique electronic properties and excellent thermal and chemical stability at room temperature have motivated researchers to use SWNTs as mandrels and to enhance their sensing capabilities through decoration of metal oxides. Such Metal Oxide/SWNTs hybrid based chemiresistors are exploited by their enhanced sensitivity and selectivity toward various gaseous analytes via charge interactions with the SWNT mandrel and by simple measurement set up.

Metal oxides have been reported as good sensing materials for various analytes\(^6\). In particular, semiconducting metal oxides such as ZnO\(^7\), SnO\(_2\)\(^8\)\(^-\)\(^10\), MoO\(_3\)\(^11\), and Ga\(_2\)O\(_3\)\(^9\)\(^,\)\(^12\) were reported as good candidates for sensing gases such as CO, NO\(_2\) and NH\(_3\) under elevated temperature. Among those metal oxides, SnO\(_2\) is commonly used to detect CO owing to its excellent surface catalytic oxidation of CO\(^13\). At elevated temperature, oxygen
vacancies are created on the oxide surface due to the chemisorption of molecular oxygen\textsuperscript{14,15}. This molecular adsorption can build up negative charges on the metal oxide surface as well as create a space charge layer. Reducing gases, such as CO and H\textsubscript{2}, donate (release) electrons to the metal oxide which increase the conductivity, while oxidizing gases, such as NO\textsubscript{2} and O\textsubscript{2}, extract electrons from the space charge layer region and create chemical bonding on the metal oxide surface which decreases the conductivity\textsuperscript{15}. SnO\textsubscript{2} is a n-type semiconductor with a wide band gap (E\textsubscript{g} = 3.6 eV), excellent chemical stability, and sensing capability which makes it a suitable transducer material in gas sensors\textsuperscript{9}. However, due to its high resistivity at ambient temperature as synthesized, SnO\textsubscript{2} as a transducer element must be operated at an elevated temperature for optimal performance\textsuperscript{8,16}. To overcome this, 1-D nanomaterials such as SWNTs are being utilized to synthesize hybrid structures for room temperature gas sensing applications\textsuperscript{17-19}. Various methods including electrospinning\textsuperscript{20}, thermal evaporation\textsuperscript{21}, and hydrothermal synthesis\textsuperscript{22} have been developed, however, their hybrid nanostructures either lack in thickness control or are in need of expensive equipment.

In this work, SnO\textsubscript{2}/SWNTs hybrid nanostructures were fabricated via AC alignment of SWNTs onto pre-fabricated microelectrodes followed by electrochemical deposition of SnCl\textsubscript{2}·2H\textsubscript{2}O and subsequent calcination in N\textsubscript{2} to form SnO\textsubscript{2} nanoparticles. Linear sweep voltammetry (LSV) was utilized to characterize the electrochemical deposition of SnO\textsubscript{2}. We demonstrated the ability to tune the sensitivity and selectivity of a SnO\textsubscript{2}/SWNTs transducer element by controlling the applied deposition potential, charge density, and the calcining temperature. The sensing performance toward NH\textsubscript{3}, CO, and
NO$_2$ under ambient condition and light illumination were correlated with the deposition conditions.

2.2 Experimental Procedure

2.2.1 Electrode Microfabrication

An individually addressable sensor array consisting of 15 microelectrodes with 3 micron gaps were microfabricated using our previously developed photolithography$^{23}$ [Figures 1(a) and (b)]. A thermally oxidized highly doped p-type Si wafer (Ultrasil Corporation, Hayward, CA) with a 300 nm oxidation layer (grown by Low Pressure Chemical Vapor Deposition) was used as the substrate. First, a positive photoresist AZ 5214-E (AZ Electronics Materials USA Corporation, Somerville, NJ) was spin-coated on the substrate at a speed of 1000 RPM for 2 s followed by 3000 RPM for 30 s, and then the substrate was placed on a hot plate at 110°C for 5 min. The patterns were photolithographically defined onto the substrates by UV light at a 70 mJ/cm$^2$ exposure dose and subsequently developed by immersing it in a developer (AZ 400K : DI water = 1 : 4, AZ Electronics Materials USA Corporation, Somerville, NJ) for 45 seconds. Afterwards, Ti (an adhesion layer) and Au films were e-beam deposited with film thicknesses of 20 nm and 180 nm, respectively. The substrate was soaked into an acetone bath overnight for the lift-off process. Prior to experiments, these prefabricated microelectrodes were diced, cleaned with acetone and water, and blown dry with ultra-high purity N$_2$ gas for further uses.
Figure 2.1 Optical images of sensor configuration: (a) patterned electrodes on a silicon wafer, (b) sensor arrays with 15 Au paired microelectrodes with 3 µm single gap as working electrodes (W.E.), integrated Au reference electrode (REF) and counter electrode (C.E.), (c) Teflon cell with pin SOIC test clips for SWNTs alignment and functionalization, and (d) customized Teflon sensing cells with gas inlet and outlet.

2.2.2 SWNTs Alignment and Functionalization

SWNTs were aligned through AC dielectrophoretic alignment\textsuperscript{24}. Carboxylated-SWNTs (SWNT-COOH 80-90% purity, Carbon Solution, Inc., Riverside, CA, USA) were first dispersed (10 µg/mL) in N,N-dimethylforamide (DMF, Sigma Aldrich, MO, USA) and sonicated for 90 minutes at room temperature until a uniform suspension was obtained.
The suspension was then transferred into a 50 mL Teflon centrifuge tube and then centrifuged for 90 minutes at 15,000 RPM at 23 °C (Beckman J2-HS and JA-17 rotor, Beckman Coulter, Inc., Brea, CA, USA). After centrifuging, 10 mL of supernatant was removed immediately and put into a glass vial. The supernatant was then sonicated for an additional 60 minutes. Afterwards, 350 µL of the supernatant was placed into the customized Teflon cell with chip holder for SWNTs alignment [Figure 1(c)]. To obtain optimal SWNTs alignment, a 2 Vpp and 4 MHz frequency was applied to the electrodes for 10 seconds. A Labview program was designed to command the Keithley 3390 AC generator (aligner) and custom-made DAQ switcher for sequential SWNTs alignment. The synthesized sensors were rinsed with DI water, dried with ultra pure N₂ gas and then calcined at 300 °C under a reducing environment (forming gas, 5% of hydrogen in nitrogen) for 1 hour to remove the residue from the solution and to improve the connection.

The SnO₂/SWNTs hybrid nanostructures were obtained by functionalizing SWNTs with electrochemical deposition of tin dioxide from an electrolyte bath containing Sn²⁺. The electrolyte for electrochemical deposition was prepared according to the previously published literature²⁵. 100 mM of sodium nitrate (≥ 99.0%, Sigma Aldrich, MO, USA) was added into 75 mM of nitric acid (70%, Sigma Aldrich, MO, USA) under constant stirring. 20 mM of tin chloride dehydrate (≥ 99.99%, Sigma Aldrich, MO, USA) was added with constant stirring for 12 hours prior to use. Finally, the pH of the solution was adjusted to 1.3 with HCl. LSV and chronoamperometry techniques were carried out at room temperature in the same customized Teflon cell with chip held [Figure 1(c)] by using a three electrode electrochemical setup. A commercial potentiostat/galvanostat (SP-200,
Potentiostat/Galvanostat/EIS, BioLogic Science Instruments, France) was used for electrochemical deposition, a Pt wire (99.99%, Sigma Aldrich, MO, USA) as the counter electrode and a saturated Ag/AgCl electrode (CHI-111, CH Instrument, Inc., Austin, TX, USA) as the reference electrode.

LSV was utilized to characterize the electrochemical deposition of tin dioxide. The ability to tune SnO$_2$ coverage and its morphology were demonstrated by controlling the applied potential and charge density. The deposition potential and charge density were optimized. The as-deposited chips were then calcined in a tube furnace at different temperatures (e.g., 400, 500 and 550 °C, respectively) in N$_2$. Decorated SWNTs devices were exposed to CO gas and the sensing performance was correlated to the coverage and morphology of the SnO$_2$ nanostructures. SnO$_2$/SWNTs hybrid nanostructures deposited at the potential of -0.55V vs. Sat. Ag/AgCl, charge density of 0.125 C/cm$^2$, and calcined at 500 °C yielded the highest sensitivity with a room temperature ppmV detection limit with fast rapid response/recovery times. The selectivity of the nanosensors was also tested by measuring its response towards NH$_3$ and NO$_2$.

2.2.3 Measurements and Material Characterization

The morphologies and compositions of the SnO$_2$/SWNTs hybrid nanostructures were investigated using field emission-scanning electron microscopy (FE-SEM, FEG-XL30, Philips) and energy-dispersive X-ray spectroscopy (EDS). The electrical resistance of these hybrid nanostructures was determined by two-probe measurements with a Keithley 236 source. Furthermore, the sensing performance of the SnO$_2$/SWNTs hybrid nanostructures was studied by installing the sensing chips in a customized sensing cell.
(maximum three chips in three separate cells at one time) with inlet and outlet ports for gas flow and then clipping the chips to a Keithley 236 source to obtain an electrical connection [Figure 1(d)]. The resistance was continuously recorded under an applied voltage fixed at 1 V. During the sensing measurement, the total gas flow rate was fixed at 200 sccm with desired analytes diluted with dry air. In all sensing experiments, sensors were first stabilized in dry air for 60 minutes, and then challenged with different concentrations of analytes with 15 minutes exposure and 20 minutes recovery times. The sensor response was determined by the resistance change before and after exposure to analyte and defined as \( \frac{R_f - R_o}{R_o} \), where \( R_f \) is the final resistance of the peak height and \( R_o \) is initial baseline resistance prior to analyte exposure. The response time is defined as the time for the sensor to reach 90% of its steady-state value, and the recovery time is identified as the time required for the sensor after the exposure to return to 50% of its maximum response.

XPS (X-ray photoelectron spectroscopy) was used to characterize the SnO\(_2\) surface chemistry. XPS data were collected with a Kratos Analytical Ultra Delay-Line Detector (DLD) imaging XPS. Aluminum K\(\alpha\) X-rays with step of 1000 meV was used to obtain the data from a 1 cm \(\times\) 1 cm chip. Phase identification was taken on Empyrean XRD (PANalytical).

In order to further investigate the light dependent property of the SnO\(_2\)/SWNTs hybrid nanostructures, the red (\(\lambda= 630\) nm, 7.2 mW, photon flux \( F = 1.44\times10^{14} /\text{cm}^2\text{s} \)), green (\(\lambda=525\) nm. 2.6 mW, photon flux \( F = 4.34\times10^{13} /\text{cm}^2\text{s} \)), and UV (\(\lambda=370\) nm, 2.5 mW, photon flux \( F = 2.98\times10^{13} /\text{cm}^2\text{s} \)) LED light (LED630E, LED525E and LED370E, Thorlabs, NJ, USA) were integrated into the customized sensing cell.
2.3 Results and Discussion

2.3.1 Fabrication, Optimization and Characterization of SnO$_2$/SWNTs Hybrid Nanostructures

LSV was performed to study the electrochemical deposition of SnO$_2$. The deposition potential was swept from +0.001 V of open circuit potential (OCP) to -1.5 V vs. a saturated Ag/AgCl reference electrode at a scan rate of 10 mV/s. Figure 2 shows typical LSV of SnO$_2$ deposition on SWNTs. Three reduction waves ($a_1$, $a_2$ and $a_3$) were observed at -0.45, and -0.55 and -0.60 V, respectively. The drop of the current around the potential of -0.35 V may attribute to the reduction of NO$_3^-$ ions which produced NH$_4^-$ and OH$^-$ ions (Eq. 1). The generated OH$^-$ ions resulted in the increasing of the local pH value which was in favor of the hydroxylation of tin precursor and led to the deposition of tin oxyhydroxide on the SWNTs. This resulted in the further increase of the current where $a_1$, $a_2$ and $a_3$ are attributed to the deposition of the tin hydroxide and the formation of the tin oxyhydroxide (Eqs. 2 and 3)$^{26}$. Since the diffusion layer has grown sufficiently on the surface of the electrode, the flux of reactant to the electrode is not fast enough to meet the deposition; therefore, the current began to drop after -0.60 V. The reduction waves at -0.95 V indicated the deposition of Sn metal. Hence, -0.45, -0.55 and -0.625 V vs. Sat. Ag/AgCl was chosen as the cathodic potential in this work. After deposition of SnO$_2$, the chip was rinsed with DI water immediately to prevent any undesirable salt residue deposited on the chip and followed by being annealed in N$_2$ at different temperature (e.g. 400, 500 and 550 °C, respectively) to form SnO$_2$ nanocrystallites (Eq. 4)$^{27}$.

\[
NO_3^- + 7 H_2O + 8 e^- \rightarrow NH_4^+ + 10 OH^- \quad \text{(Eq.1)}
\]
\[ Sn^{2+} + 2OH^- \rightarrow Sn(OH)_2 \]  
(Eq.2)

\[ Sn(OH)_2 - xH_2O \rightarrow SnO_{1+x}(OH)_{2-2x} \]  
(Eq.3)

\[ SnO_{1+x}(OH)_{2-2x} \rightarrow SnO_2 \]  
(Eq.4)

Figure 2.2 (a) Linear sweep voltammetry (LSV) of SnO2 deposition on SWNTs and (b) Transient curve for SnO2 deposition at -0.45 (black), -0.55 (red) and -0.625 V (blue) vs. Sat. Ag/AgCl with charge density of 0.25 C/cm². Electrolyte: 100 mM of NaNO₃, 75 mM of HNO₃, and 20 mM of SnO₂·H₂O. Total solution volume was fixed at 700 µL. LSV was performed with a fixed scan rate of 10 mV/s at room temperature.

Chronoamperometry was conducted at the fixed cathodic potential of -0.45, -0.55, and -0.625 V vs. Sat. Ag/AgCl, respectively, for the deposition process which was controlled by the charge applied. The effects of the deposition charge density on the electrical properties and sensing performance of the SnO2 functionalized SWNTs (SnO2/SWNTs hybrid nanostructures) were systematically investigated. FE-SEM was used to inspect the SnO2/SWNTs hybrid nanostructures which were deposited at different deposition potentials (-0.45, -0.55, and -0.625 V vs. Sat. Ag/AgCl, respectively) and charge densities (0.0125 C/cm², 0.125 C/cm² and 0.25 C/cm², respectively), [Figures 3(a)-(i)]. There was barely SnO₂ when the deposition charge density was 0.0125 C/cm² [the left
column in Figure 3]. As the deposition charge increasing, more SnO$_2$ particles were deposited. When the charge density reached 0.125 C/cm$^2$, SnO$_2$ particles was deposited in moderate density [the middle column in Figure 3], while when the charge density reached 0.25 C/cm$^2$, SnO$_2$ was deposited in a very high density [the right column in Figure 3]. As demonstrated in the SEM images, SnO$_2$ was not selectively deposited on top of SWNTs but everywhere on the surface, which indicated the formation of a uniform and continuous SnO$_2$ film on the whole substrate during the deposition. The EDX result was shown in Figure 4, from which we can clearly see the composition of the film, Sn and O from SnO$_2$, C and O from the SWNTs, and Au from the electrodes.
**Figure 2.3** SEM images of SnO$_2$/SWNTs hybrid nanostructures at different electrochemical deposition potential and charge density (a) potential: -0.45 V vs. Sat. Ag/AgCl, charge density: 0.0125 C/cm$^2$, (b) potential: -0.45 V vs. Sat. Ag/AgCl, charge density: 0.125 C/cm$^2$, (c) potential: -0.45 V vs. Sat. Ag/AgCl, charge density: 0.25 C/cm$^2$, (d) potential: -0.55 V vs. Sat. Ag/AgCl, charge density: 0.0125 C/cm$^2$, (e) potential: -0.55 V vs. Sat. Ag/AgCl, charge density: 0.125 C/cm$^2$, (f) potential: -0.55 V vs. Sat. Ag/AgCl, charge density: 0.25 C/cm$^2$, (g) potential: -0.625 V vs. Sat. Ag/AgCl, charge density: 0.0125 C/cm$^2$, (h) potential: -0.625 V vs. Sat. Ag/AgCl, charge density: 0.125 C/cm$^2$, and (i) potential: -0.625 V vs. Sat. Ag/AgCl, charge density: 0.25 C/cm$^2$, respectively.
The room temperature back-gated FET measurements were carried out in order to study the electrical transfer characteristics of the SWNTs and SnO$_2$/SWNTs hybrid nanostructures. Figure 5 is the output of source-drain current ($I_{SD}$) versus gate voltage ($V_G$) at fixed voltage ($V_{SD}$) characteristics FET measurements. All the sensors except the SnO$_2$/SWNTs hybrid nanostructures deposited at the charge density of 0.25 C/cm$^2$ exhibited typical p-type semiconducting behavior\textsuperscript{2}. The SWNTs used in this work is a mixture of metallic and semiconductor SWNTs, which showed lower on/off ratio ($I_{on}/I_{off} = 2.6$) compared with previously reported results\textsuperscript{2}. The deteriorated transport properties were observed after SWNTs functionalization, showing neither on nor off values. However, the conductivity did increase with increased deposition charge density and greater SnO$_2$ coverage. This is believed to be due to the p-n junction formed between the p-type SWNTs and n-type SnO$_2$ semiconductors. The very different band gaps, 0.57 eV and 3.6 eV\textsuperscript{28}, but
similar work functions, 5.0 eV and 4.8 eV\textsuperscript{28} for SWNTs and SnO\textsubscript{2}, respectively, are believed to create barriers for charge carrier transport between the two materials. This resulted in parallel current flow through the SnO\textsubscript{2} particles, correlating well with the increased conductivity for greater SnO\textsubscript{2} coverage. The weakened gate dependence is an expected result of the increased coverage of SnO\textsubscript{2} as the gate field does not penetrate their cross section as strongly but more importantly the more SnO\textsubscript{2} particles disrupt highly homo-semiconductive channel formation. Moreover, the low hole mobility and high conductivities of the functionalized SWNTs are also in agreement with the SnO\textsubscript{2} dominated conduction mechanism as the high carrier concentration of SnO\textsubscript{2} with respect to SWNTs permits the observed conductivities. Very interestingly, the SnO\textsubscript{2}/SWNTs hybrid structures formed at the highest deposition charge density of 0.25 C/cm\textsuperscript{2} demonstrated some weak n-type semiconducting behavior. This might be attributed to the complete enclosure of the SWNTs by SnO\textsubscript{2}, where the electrons became the main charge carriers. This strategy could be used as a leverage to modulate the p-type and n-type semiconductor based devices in the future work.
Figure 2.5 Electron transfer characteristics [Current (I_{SD}) vs. back gated voltage (V_G)] of AC aligned SWNTs (black) and SnO_2/SWNTs hybrid nanostructures deposited at the potential of (a) -0.45, (b) -0.55 and (c) -0.625 V vs. Sat. Ag/AgCl [red, blue and magenta represent the responses acquired from hybrid structures shown in Figures 3(a), (b) and (c), respectively]. The source-drain potential (V_{SD}) was fixed at 1 V and measurements were conducted at room temperature in air.

2.3.2 Sensing Performance of SnO_2/SWNTs Hybrid Nanostructures at Room Temperature in the Absence of Light

2.3.2.1 Carbon Monoxide Sensing Performance

Figures 6, 7, and 8 show the normalized resistance change of the SnO_2/SWNTs hybrid nanostructures deposited at charge densities of 0.0125, 0.125, and 0.25 C/cm^2, respectively, each at the three potentials and annealing temperatures of -0.45 V, -0.55 V, -0.625 V and 400 °C, 500 °C, 550 °C, respectively, as a function of CO concentration. In nearly all cases, the SnO_2/SWNTs hybrid nanostructures sensing performance improved with respect to the bare SWNTs - which barely showed any response toward CO\textsuperscript{28}. As shown in Figure 6, i), when the deposition charge density was fixed at 0.0125 C/cm^2, the SnO_2/SWNTs hybrid nanostructures deposited at -0.55 V showed the highest sensing response regardless of the annealing temperature, and ii) when the deposition charge
density and potential are held constant, the SnO$_2$/SWNTs hybrid nanostructures annealed at 500 °C clearly stood out showing the highest sensing response with the least noise in the signal. These same observations hold true for the higher charge densities shown in Figures 7 and 8, namely, i) the SnO$_2$/SWNTs hybrid nanostructures deposited at -0.55 V showed the highest sensing response regardless of the annealing temperature, and ii) when the deposition charge density and potential were held constant, the SnO$_2$/SWNTs hybrid nanostructures annealed at 500 °C showed the highest sensing response with the least signal noise.

For example, at the deposition charge density of 0.125 C/cm$^2$, the normalized sensor response for 200 ppm$_v$ CO was 10% when annealed at 500 °C (Figure 7) vs 1.3% at 400 °C and 3.2% at 550 °C. Figure 9 shows the sensing response towards CO for the three conditions investigated in a 3D bar plot. This plot clearly depicts that when other parameters are held constant, the SnO$_2$/SWNTs hybrid nanostructures fabricated at 0.125 C/cm$^2$, -0.55 V and annealed at 500 °C yields the optimum sensing response. This is consistent with our SEM results (Figure 3) showing moderate deposition density of SnO$_2$ at the charge density of 0.125 C/cm$^2$. The SnO$_2$/SWNTs hybrid nanostructures prepared with optimum condition was further challenged with different concentrations of CO as low as 5 ppm$_v$. As shown in Figure 10(a), such nanostructures responded linearly at a lower CO concentration (5 – 100 ppm$_v$) and nearly reached saturation when the CO concentration exceeded 100 ppm$_v$. The saturation is due to CO occupying sites where oxygen molecules originally bonded. The reduction in the surface adsorbed oxygen concentration and

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inhibiting its re-absorption severely restrains the oxidation reaction of CO into CO\(_2\) causing SnO\(_2\) surface poisoning\(^{29}\)
Figure 2.6 Real-time sensing performance and its corresponding calibration curve of SnO$_2$/SWNTs hybrid nanostructures toward CO at the Calcination temperature of (a) 400, (b) 500 and (c) 550 °C, respectively [Deposition charge density: 0.0125 C/cm$^2$; and Deposition potential: -0.45 (black), -0.55 (red), and -0.625 V (blue) vs. Sat. Ag/AgCl, respectively].
Figure 2.7 Real-time sensing performance and its corresponding calibration curve of SnO$_2$/SWNTs hybrid nanostructures toward CO at the annealing temperature of (a) 400, (b) 500 and (c) 550 °C, respectively [Deposition charge density: 0.125 C/cm$^2$; and Deposition potential: -0.45 (black), -0.55 (red), and -0.625 V (blue) vs. Sat. Ag/AgCl, respectively].
Figure 2.8 Real-time sensing performance and its corresponding calibration curve of SnO$_2$/SWNTs hybrid nanostructures toward CO at the Calcination temperature of (a) 400, (b) 500 and (c) 550 °C, respectively [Deposition charge density: 0.25 C/cm$^2$; and Deposition potential: -0.45 (black), -0.55 (red), and -0.625 V (blue) vs. Sat. Ag/AgCl, respectively].
Figure 2.9 Correlation of the SnO$_2$/SWNTs hybrid nanostructures sensing performance toward CO. Deposition charge density was fixed at (a) 0.0125, (b) 0.125 and (c) 0.25 C/cm$^2$, respectively [Deposition potential: -0.45, -0.55 and -0.625 V vs. Sat. Ag/AgCl, respectively; and annealing temperature: 400 (yellowgreen), 500 (orange) and 550 ºC (darkred), respectively]. The optimum condition for CO sensing: deposition potential at -0.55 V vs. Sat. Ag/AgCl, charge density at 0.125 C/cm$^2$, and annealing temperature at 500 ºC.
2.3.2.1.1 Carbon Monoxide Sensing Mechanism

To understand the sensing mechanism of the SnO$_2$/SWNTs hybrid nanostructure toward CO, one must envision the reaction of CO molecules in the gas phase with adsorbed oxygen molecules$^{29-31}$ on the adsorbent SnO$_2$ surface. The two most popular surface reaction mechanisms cited are the Langmuir-Hinselwood mechanism$^{29}$ (L-H) and the Eley-Rideal mechanism$^{32}$ (E-R). In the L-H mechanism, a CO molecule in the gas phase is first adsorbed onto the SnO$_2$ surface, where it eventually reacts with a surface adsorbed oxygen molecule to form the product CO$_2$ which is released to the air under the assumption of an isothermal steady state condition. In the E-R mechanism, a CO molecule in the gas phase reacts directly with a previously adsorbed oxygen molecule, without being adsorbed itself, to release the product CO$_2$ into the air resulting in a nonthermal surface reaction. The resulting rate law is typically complex, where both mechanisms may be active. Thus, the
exact sequence of events is not clear, but we should keep in mind that the global reaction rate for both mechanisms is first order with respect to CO at atmospheric pressure\textsuperscript{29}.

One comparison to be noted is that the conductivity of our SnO\textsubscript{2}/SWNTs hybrid nanostructure decreases when exposed to CO, whereas, the conductivity of a thick/thin film SnO\textsubscript{2} sensor\textsuperscript{9} increases upon CO exposure. This is because the SWNTs are p-type semiconductors with holes as its major charge carrier, whereas electrons are the major charge carriers in a thick/thin SnO\textsubscript{2} film. Thus, the released electron in the CO to CO\textsubscript{2} reaction would add to the majority charge carriers in a thick/thin SnO\textsubscript{2} film, thus increasing its conductivity, but it would recombine with holes reducing their number in the SWNTs, thus decreasing its conductivity. This explanation is consistent with previous work\textsuperscript{28}.

XRD was used to further understand the microstructure of the optimum condition. Figure 11 compares three XRD patterns on the SnO\textsubscript{2} thin film deposited at -0.55 V at 0.125 C/cm\textsuperscript{2} and calcined four hours at 400 °C, 500 °C, and 550 °C in N\textsubscript{2}. The figure clearly shows that as the calcining temperature increased from 400 °C to 500 °C, the degree of crystallinity increased as did its CO sensing performance\textsuperscript{29}. However, the sensing performance declined for the third sample calcined at 550 °C. This may be due to grain growth of the SnO\textsubscript{2} particles, lowering the overall surface area; therefore, reducing its CO sensing performance by decreasing the active SnO\textsubscript{2} sensing sites.
Figure 2.11 XRD pattern of the SnO$_2$ thin film deposited at -0.55 V vs. Sat. Ag/AgCl and calcinated under (a) 400 °C (black), (b) 500 °C (red), and (c) 550 °C (blue) in N$_2$ for 4 hours. The peak with the open circle symbols are the peaks of substrate (SiO$_2$/Si). The spectrum have been vertically shifted for clarity.

### 2.3.2.2 Ammonia Sensing Performance

There are many reports in the literature on the detection of ammonia by means of electrospun conducting polymers$^{33}$, by metal oxides$^{34-36}$, and by conducting polymer/metal oxide composites$^{37}$, but there are limited reports on sensing NH$_3$ by means of SnO$_2$/SWNTs hybrid nanostructures operated at room temperature. In this work, the SnO$_2$/SWNTs hybrid nanostructures were tested against ammonia under ambient condition. Figures 12-14 show the sensor response (percent change in normalized resistance) of the SnO$_2$/SWNTs hybrid
nanostructures deposited at the three cathodic potentials of -0.45, -0.55, -0.625 V, respectively, each run under three controlling charge densities of 0.0125, 0.125, and 0.25 C/cm² and three post annealing temperatures of 400, 500, and 550 °C as a function of NH₃ concentration.

As shown in Figure 12, i), when the deposition charge density was fixed at 0.0125 C/cm², the SnO₂/SWNTs hybrid nanostructures deposited at the most negative potential at -0.625 V showed the highest sensing response regardless of the annealing temperature, and ii) when the deposition charge density and potential are held constant, the SnO₂/SWNTs hybrid nanostructures annealed at the lowest temperature of 400 °C showed the highest sensing response at the higher NH₃ concentration but no response at lower NH₃ concentrations; while those annealed at 500 °C and 550 °C showed a response even when the NH₃ concentration was low.

These same observations hold true for the higher charge densities shown in Figures 13 and 14. Figure 15 shows 3-D bar plots revealing all three conditions at once for NH₃ sensing clearly showing in a glance the trends mentioned above. For example, the sensor response fabricated under the three conditions (-0.625 V, 0.125 C/cm², 400 °C) to a 50 ppm NH₃ exposure decreased from 53% to 32% when the annealing temperature increased from 400 °C to 550 °C [Figures 13(a) and 13(c), respectively], and its sensitivity of 1.05%/ppm (Figure 13) dropped to 0.71%/ppm at 0.0125 C/cm² (Figure 12) and to 0.88%/ppm at 0.25 C/cm² (Figure 14). Based on this limited study, the fabrication method at (-0.625 V, 0.125 C/cm², 400 °C) yielded the best sensitivity for the SnO₂/SWNTs hybrid nanostructures for sensing NH₃ at room temperature.
Figure 2.12 Real-time sensing performance and its corresponding calibration curve of SnO$_2$/SWNTs hybrid nanostructures toward NH$_3$ at the calcination temperature of (a) 400, (b) 500 and (c) 550 °C, respectively [Deposition charge density: 0.0125 C/cm$^2$; and Deposition potential: -0.45 (black), -0.55 (red), and -0.625 V (blue) vs. Sat. Ag/AgCl, respectively].
Figure 2.13 Real-time sensing performance and its corresponding calibration curve of SnO₂/SWNTs hybrid nanostructures toward NH₃ at the Calcination temperature of (a) 400, (b) 500 and (c) 550 °C, respectively [Deposition charge density: 0.125 C/cm²; and Deposition potential: -0.45 (black), -0.55 (red), and -0.625 V (blue) vs. Sat. Ag/AgCl, respectively].
Figure 2.14 Real-time sensing performance and its corresponding calibration curve of SnO$_2$/SWNTs hybrid nanostructures toward NH$_3$ at the Calcination temperature of (a) 400, (b) 500 and (c) 550 °C, respectively [Deposition charge density: 0.25 C/cm$^2$; and Deposition potential: -0.45 (black), -0.55 (red), and -0.625 V (blue) vs. Sat. Ag/AgCl, respectively].
Figure 2.15 Correlation of the SnO$_2$/SWNTs hybrid nanostructures sensing performance toward NH$_3$. Deposition charge density was fixed at (a) 0.0125, (b) 0.125 and (c) 0.25 C/cm$^2$, respectively [Deposition potential: -0.45, -0.55 and -0.625 V vs. Sat. Ag/AgCl, respectively; and annealing temperature: 400 (yellowgreen), 500 (orange) and 550 °C (darkred), respectively]. The optimum condition for NH$_3$ sensing: deposition potential at -0.625 V vs. Sat. Ag/AgCl, charge density at 0.125 C/cm$^2$, and annealing temperature at 400 °C.
2.3.2.2.1 Ammonia Sensing Mechanism

As shown in Figures 12-14, the resistance of the SnO$_2$/SWNTs hybrid nanostructures increased when exposed to NH$_3$. This is in line with work by Li et al.,$^{36}$ and Abee et al.,$^{38}$ asserting that NH$_3$ molecules are electron donors, and they can bind to a SnO$_2$ surface through the lone pair on the nitrogen atom of NH$_3$. The donated electrons enhance the conductivity of the n-type SnO$_2$ metal oxide, but they decrease the conductivity of the p-type SWNTs by recombining with holes, thus reducing the concentration of the major charge carrier. Figure 3 displays SEM images of the changes in the SnO$_2$/SWNTs hybrid morphology as a function of deposition potential and charge density. As can be seen, the most notable change in morphology is with respect to increasing charge density. In general, the most negative potential of -0.625 V and the lowest calcining temperature of 400 °C yielded the highest sensing responses, but the system showed its optimal response under the intermediate 0.125 C/cm$^2$ charge density. This can be explained from the LSV curve (Figure 2), where SnO$_2$ was formed between the peak a1 (-0.45 V) and a3 (-0.6 V), Sn metal was formed when the potential was more negative than -0.8 V, and the formation of SnO was favored when the potential was between -0.6 and -0.8 V. Therefore, particles of SnO instead of SnO$_2$ were deposited on SWNTs at the deposition potential of -0.625 V. This is in line with work by Abee et al.,$^{38}$ asserting that NH$_3$ molecules have a higher affinity to the four coordinate Sn$^{2+}$ cation than to the Sn$^{4+}$ cation due to the former’s larger heat of adsorption.

XPS and XRD were performed to further investigate this phenomenon. Figure 16 is the XPS survey spectrum of SnO$_2$ thin films on Au/SiO$_2$ chips, heat treated at 400 °C in
N₂, and measured under deposition potentials of (a) -0.45 V; (b) -0.55 V and (c) -0.625 V vs. Sat. Ag/AgCl, respectively. From the high resolution XPS spectra of Sn in Figure 17 and the corresponding peak area ratio in Table 1, an increasing formation of Sn²⁺ was observed at deposition potentials between -0.45 to -0.625 V. The XRD pattern in Figure 18 shows the presence of a SnO peak which is consistent with the XPS result. Figure 18(a) shows that as the deposition potential becomes more negative, the SnO peak becomes more pronounced; while Figure 18(b) shows that increasing the calcining temperature from 400 °C to 550 °C, the SnO fully transformed into SnO₂. On the other hand, the lower sensing response of the SnO₂/SWNTs hybrid nanostructures calcined at the higher temperature could be explained as grain growth of the SnO₂ nanoparticles which would lead to a decline in active binding sites for the NH₃ molecules.

It is somewhat reassuring that the optimal NH₃ sensing performance of the SnO₂/SWNTs hybrid system under the fabrication parameters of (-0.625 V, 0.125 C/cm²) has a morphology that can be identified amongst SEM micrographs as displayed in Figure 3. For example, when the deposition charge density is higher at 0.25 C/cm², one can easily see a rather thick film of SnO₂ which would lead to a decline in surface area and active binding sites for oxygen adsorption, and at a lower charge density of 0.0125 C/cm², only a few small nuclei of tin with diameters around 30 nm are visible, again, providing too little a surface area for optimal gas adsorption. A similar visual examination can narrow the range for the optimal cathodic potential setting.
Figure 2.16 XPS survey spectrum of SnO$_2$ thin films on Au/SiO$_2$ chip, heat treated at 400 °C in N$_2$, measured on deposition potentials of (a) -0.45 V; (b) -0.55 V and (c) -0.625 V vs. Sat. Ag/AgCl. The spectrum have been vertically shifted for clarity.
Figure 2.17 XPS spectra of (a) Sn 3d and (b) Sn 3d$_{5/2}$ for the SnO$_2$ thin film after 400 °C calcination in N$_2$. The open black square, red circle and blue star symbols are the SnO$_2$ thin films deposited at -0.45, -0.55, and -0.625 V respectively.
Figure 2.18 XRD pattern for the heat treated SnO\textsubscript{2} thin film from the electrochemical deposition process: (a) SnO\textsubscript{2} thin film deposited at -0.45 (black), -0.55 (red), and -0.625 V (blue) vs. Sat. Ag/AgCl (calcinated under 400 °C in N\textsubscript{2} environment); (b) SnO\textsubscript{2} thin film deposited at -0.625 V vs. Sat. Ag/AgCl and calcinated under 400 (black), 500 (red), and 550 °C (blue) in N\textsubscript{2}. The peaks with open circle symbols are the peaks of the substrate (SiO\textsubscript{2}/Si). The spectrum have been vertically shifted for clarity.

<table>
<thead>
<tr>
<th>Deposition potential vs. Sat. Ag/AgCl (V)</th>
<th>O/Sn peak area ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.45</td>
<td>0.58</td>
</tr>
<tr>
<td>-0.55</td>
<td>0.55</td>
</tr>
<tr>
<td>-0.625</td>
<td>0.51</td>
</tr>
</tbody>
</table>

### 2.3.2.3 Nitrogen Dioxide sensing performance

In this work, the various SnO\textsubscript{2}/SWNTs hybrid nanostructures were tested against nitrogen dioxide under ambient condition and were optimized to obtain the best sensing result. Figures 19-21 show the sensor response (percent change in normalized resistance) of the SnO\textsubscript{2}/SWNTs hybrid nanostructures deposited at the three cathodic potentials of -
0.45, -0.55, -0.625 V, respectively, each run under three controlling charge densities of 0.0125, 0.125, and 0.25 C/cm$^2$ and three post annealing temperatures of 400, 500, and 550 °C as a function of NO$_2$ concentration.

As shown in Figure 19, i) when the deposition charge density was fixed at its lowest of 0.0125 C/cm$^2$, the SnO$_2$/SWNTs hybrid nanostructures deposited at the intermediate potential of -0.55 V showed the highest sensing response regardless of their annealing temperature; and ii) when the deposition charge density and potential are held constant, the hybrid nanostructures annealed at 400 °C showed the largest response at both the highest and lowest NO$_2$ concentrations with the capability of sensing NO$_2$ down to 0.1 ppm; while those annealed at 500 and 550 °C showed no response at low NO$_2$ concentrations. This is also true at the higher charge density of 0.125 C/cm$^2$, Figure 20. In the case of the highest charge density the sensing performance changed. At the deposition potential of -0.45 V at 0.25 C/cm$^2$, the SnO$_2$/SWNTs hybrid nanostructures behaved as a typical thin/thick film SnO$_2$ sensor$^{39}$. This is because, as shown in the SEM image in Figure 3(c), the sensing behavior is the result of a bulk SnO$_2$ film - not the combination of the SnO$_2$/SWNTs hybrid nanostructure. At the deposition potentials of -0.55 and -0.625 V, SWNTs were not fully covered by SnO$_2$ and there were some SnO$_2$ aggregations, which altered the electrical properties and caused the unexpected sensing results.
Figure 2.19 Real-time sensing performance and its corresponding calibration curve of SnO$_2$/SWNTs hybrid nanostructures toward NO$_2$ at the Calcination temperature of (a) 400, (b) 500 and (c) 550 °C, respectively [Deposition charge density: 0.0125 C/cm$^2$; and Deposition potential: -0.45 (black), -0.55 (red), and -0.625 V (blue) vs. Sat. Ag/AgCl, respectively].
Figure 2.20 Real-time sensing performance and its corresponding calibration curve of SnO$_2$/SWNTs hybrid nanostructures toward NO$_2$ at the Calcination temperature of (a) 400, (b) 500 and (c) 550 °C, respectively [Deposition charge density: 0.125 C/cm$^2$; and Deposition potential: -0.45 (black), -0.55 (red), and -0.625 V (blue) vs. Sat. Ag/AgCl, respectively].
Figure 2.21 Real-time sensing performance and its corresponding calibration curve of SnO$_2$/SWNTs hybrid nanostructures toward NO$_2$ at the Calcination temperature of (a) 400, (b) 500 and (c) 550 °C, respectively [Deposition charge density: 0.25 C/cm$^2$; and Deposition potential: -0.45 (black), -0.55 (red), and -0.625 V (blue) vs. Sat. Ag/AgCl, respectively].
2.3.2.4 Nitrogen Dioxide Sensing Mechanism

NO\textsubscript{2} has been identified as a strong electron-withdrawing molecule\textsuperscript{1}, which once adsorbed onto the surface of a metal oxide it can reduce the metal’s conducting electron density thus decreasing its conductivity. The mechanism of NO\textsubscript{2} sensing for our SnO\textsubscript{2}/SWNTs hybrid nanostructures can be described as its chemisorption onto SWNTs, and onto the SnO\textsubscript{2} surface, especially onto defect sites on the SnO\textsubscript{2} surface, followed by an interfacial electron transfer\textsuperscript{40}. The XRD pattern in Figure 11 shows that the degree of crystallinity of a SnO\textsubscript{2} film increased as the calcination temperature increased, and calcination is typically associated with a decrease in surface defect sites. Such a decrease in defect sites is in line with our NO\textsubscript{2} sensing results where the SnO\textsubscript{2}/SWNTs hybrid nanostructures showed the best sensing results when i) calcined at the lowest temperature of 400 °C-retaining its defect sites, and ii) deposited at 0.125 C/cm\textsuperscript{2}-yielding the highest SnO\textsubscript{2} surface area on SWNTs. A 3-D plot of the NO\textsubscript{2} sensing results are shown in Figure 22.
Figure 2.22 Correlation of the SnO$_2$/SWNTs hybrid nanostructures sensing performance toward NO$_2$. Deposition charge density was fixed at (a) 0.0125, (b) 0.125 and (c) 0.25 C/cm$^2$, respectively [Deposition potential: -0.45, -0.55 and -0.625 V vs. Sat. Ag/AgCl, respectively; and annealing temperature: 400 (yellow green), 500 (orange) and 550 °C (dark red), respectively]. The optimum condition for NO$_2$ sensing: deposition potential at -0.55 V vs. Sat. Ag/AgCl, charge density at 0.125 C/cm$^2$, and annealing temperature at 400 °C.
2.3.3 Carbon Monoxide, Ammonia, and Nitrogen Dioxide Sensing under LED Lights Illumination

SnO$_2$ as an n-type semiconducting oxide with a wide band gap (3.62 eV) has been utilized in fabricating light harvesting devices$^{41,42}$. SnO$_2$ based hybrid architectures have also been demonstrated as promising components for light sensitive/ harvesting materials. Herein we investigated the effect of light exposure to our SnO$_2$/SWNTs hybrid nanostructures against NH$_3$, CO, and NO$_2$ sensing. The SnO$_2$/SWNTs hybrid nanostructures were prepared at the optimum condition for each gas as noted above.

Photoelectrical measurements of the SnO$_2$/SWNTs hybrid nanostructures were carried out with red (630 nm, 7.2mW, photon flux $F = 1.44 \times 10^{14}$/cm$^2$s), green (525 nm, 2.6 mW, photon flux $F = 4.34 \times 10^{13}$/cm$^2$s), and UV (370 nm, 2.5 mW, photon flux $F = 2.98 \times 10^{13}$/cm$^2$s) LED lights, respectively. The ohmic contact I-V characteristics shown in Figure 23(a) indicated that the response under light illumination came from the hybrid structures- not from the external contact. In addition, the current passing through the hybrid structures decreased under light illumination. This is in line with the FET result, where the current dropped significantly under light illumination compared to the one measured under ambient conditions, Figure 23(b). Figure 24 shows the typical transient photo current response of bare SWNTs under UV light, and the SnO$_2$/SWNTs hybrid nanostructures under red, green, and UV lights, respectively. The current of the SWNTs (Figure 24(a)) decreased about 6% upon the illumination of the UV light (where $\Delta I/I_o$ is defined as the difference between the illuminated and dark current values divided by the dark current), then slowly recovered after the light was turned off. The decrease in current upon
illuminating SWNTs was due to oxygen photodesorption, which led to a reduction in the hole carrier concentration; thus, lowering the conductance of the p-type SWNTs\textsuperscript{43}. In the system of SnO\textsubscript{2}/SWNTs hybrid nanostructures, two processes have been reported to occur in the metal oxide upon LED light exposure. Firstly, photons whose energy exceeds the band gap energy of SnO\textsubscript{2} (such as UV photons) can photogenerate electron-hole pairs\textsuperscript{44} (Equation 5). Secondly, there is photodesorption of surfaced adsorbed oxygen molecules (Equation 6)\textsuperscript{43,44}.

\begin{align}
    hv & \rightarrow e^- + h^+ \quad \text{(Eq.5)} \\
    O_2^-(ad) + h^+ & \rightarrow O_2(g) \quad \text{(Eq.6)} \\
    O_2(g) + e^- & \rightarrow O_2^- (ad) \quad \text{(Eq.7)}
\end{align}

Although red (\(\lambda = 630\ \text{nm} \sim 2\text{eV}\)) and green light (\(\lambda = 525\ \text{nm} \sim 2.36\text{eV}\)) photons do not exceed the band gap energy of SnO\textsubscript{2} (3.6 eV), the current decreased with the illumination of red and green light as shown in Figure 24(b) and (c), respectively. This is due to the adsorbed surface oxygen molecules leaving excess electrons in the SWNTs where they recombined with the holes; thus, decreasing the number of major charge carriers of the SWNTs. In the case of UV light illumination [Figure 24(d)], a significant current decrease of around 25\% was observed, owing to both the photodesorption of surface adsorbed oxygen and the flow of the excess electrons generated from the SnO\textsubscript{2}. After turning off the light, i) the free electrons generated by photo excitation were consumed by the recombination with holes, ii) the oxygen molecules would reabsorb from the ambient atmosphere to the surface of the hybrid structures and withdraw the electrons. These resulted in the recovery of the current flow\textsuperscript{43}. 

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Figure 2.23 (a) I-V characteristics and (b) field effect transfer characteristics of SnO$_2$/SWNTs hybrid nanostructures synthesized at -0.55 V vs. Sat. Ag/AgCl with charge density of 0.125 C/cm$^2$ and calcinated at 500 °C in N$_2$. In both figures, black solid line measured in dark, red short dash dot measured under red, green short dot measured under green and purple dash line measured under UV illumination.
Figure 2.24 Transient photocurrent response of bare SWNTs under (a) UV light (370 nm, 2.5 mW), SnO$_2$/SWNTs hybrid nanostructures under (b) red light, (c) green light, and (d) UV light, respectively. Shaded areas indicate the exposure of the LED light.

Figure 25 shows the CO sensing performance (from 5 to 200 ppmv) under UV illumination. The UV light was left on during the entire sensing process. Here we can observe that under UV illumination the sensing performance was significantly enhanced (a 7% to 18 % change at PEL = 50 ppm) with better recovery. The enhancement is due to the photodesorption of surface oxygen under UV illumination leaving more binding sites for CO. Therefore, the oxidation rate of the CO on the SnO$_2$ surface increased. The enhanced CO oxidation rate resulted in excess electron flow into the SnO$_2$/SWNTs hybrid nanostructures causing an increase in resistance. However, the sensor reached saturation
When the CO concentration exceeded 50 ppmv. The saturation might be due to the fullness of CO binding sites on SnO$_2$ leading to the poisoning of the SnO$_2$ surface. Figure 26 shows that under the assistance of UV light, the detection limit of these SnO$_2$/SWNTs hybrid nanostructures toward CO can be pushed down to 0.5 ppmv. This is because the photodesorption of the surface oxygen and thus the CO molecules can bind with the SnO$_2$ surface without the competition of the oxygen molecules. This photodesorption phenomenon can also explain the enhancement toward NH$_3$ and NO$_2$ sensing under UV illumination as shown in Figure 27 and 28. The sensing performance toward NH$_3$ was enhanced from 50% to 80% at PEL = 50 ppm. The sensing performance toward NO$_2$ did not show significant enhancement, but the recovery after the termination of the NO$_2$ gas was improved. This is because the photogenerated holes recombined with the electrons trapped by NO$_2$ on the surface leading to the desorption of NO$_2$. In general, the sensitivity, response time and recovery time were improved under UV illumination compared with those measured under ambient conditions. The detailed information is listed in the Table 2.2.

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Figure 2.25 (a) Real-time sensing performance and (b) its corresponding calibration curve of SnO$_2$/SWNTs hybrid nanostructures toward CO (5-200 ppm) under in dark and UV LED (370 nm, 2.5 mW, photon flux $F = 2.98 \times 10^{13}$ /cm$^2$s) illumination, respectively [Deposition charge density: 0.125 C/cm$^2$, Deposition potential: -0.55 vs. Sat. Ag/AgCl, and annealing temperature: 500 °C].

Figure 2.26 (a) Real-time sensing performance and (b) its corresponding calibration curve of SnO$_2$/SWNTs hybrid nanostructures toward CO (0.5-5 ppm) under UV LED illumination (370 nm, 2.5 mW, photon flux $F = 2.98 \times 10^{13}$ /cm$^2$s) [Deposition charge density: 0.125 C/cm$^2$, Deposition potential: -0.55 vs. Sat. Ag/AgCl, and annealing temperature: 500 °C].
Figure 2.27 Real-time sensing performance and its corresponding calibration curve of SnO$_2$/SWNTs hybrid nanostructures toward NH$_3$ (0.5-100 ppm) under UV LED (370 nm, 2.5 mW, photon flux $F = 2.98 \times 10^{13}$ /cm$^2$s) illumination, respectively [Deposition charge density: 0.125 C/cm$^2$, Deposition potential: -0.625 vs. Sat. Ag/AgCl, and annealing temperature: 400 °C].

Figure 2.28 Real-time sensing performance and its corresponding calibration curve of SnO$_2$/SWNTs hybrid nanostructures toward NO$_2$ (0.1-10 ppm) under UV LED (370 nm, 2.5 mW, photon flux $F = 2.98 \times 10^{13}$ /cm$^2$s) illumination, respectively [Deposition charge density: 0.125 C/cm$^2$, Deposition potential: -0.55 vs. Sat. Ag/AgCl, and annealing temperature: 500 °C].
Table 2.2 Sensing properties of the optimized SnO$_2$/SWNTs hybrid nanostructures toward CO, NH$_3$ and NO$_2$ at PEL level of 50, 50, and 5 ppm, room temperature in the ambient condition and under UV illumination, respectively.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Sensitivity (% ppm$^{-1}$)</th>
<th>Response Time $t_{90}$ (mins)</th>
<th>Recovery Time $t_{50}$ (mins)</th>
<th>Operation Temperature ($^\circ$C)</th>
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</tr>
<tr>
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<td>10.8</td>
<td>16.3</td>
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<td>NO$_2$</td>
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<td>10.2</td>
<td>13.1</td>
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<td>Under UV Illumination</td>
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<tr>
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<td>7.4</td>
<td>6.9</td>
<td>R.T.</td>
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<tr>
<td>NO$_2$</td>
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<td>8.1</td>
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2.4 Conclusions

SnO$_2$/SWNTs hybrid nanostructure based chemiresistive sensors toward gaseous analytes were synthesized by AC alignment of SWNTs followed by electrochemical deposition of SnO$_2$ by independently controlling Voltage vs. Sat. Ag/AgCl and deposition charge density, followed by calcination of the hybrid structure- simply abbreviated by (V, C/cm$^2$, °C), respectively. SnO$_2$ was chosen because it can provide active reaction sites for several different kinds of analytes, and SWNTs semiconductors were selected for their excellent electrical, thermal and chemical stability at room temperature. The morphology and coverage of the SnO$_2$ nanoparticles were controlled by adjusting the deposition potential and charge density, and post annealing of the nanostructures was done at 400 °C, 500 °C, and 550 °C to determine its effect on sensor sensitivity as chemiresistors. The
selectivity of the gas sensors was determined by analyzing their response to CO, NH₃, and NO₂ exposure at room temperature. We found optimal sensitivity at room temperature under the conditions (-0.55 V, 0.125 C/cm², 500 °C) for CO and NH₃, and at (-0.55 V, 0.125 C/cm², 400 °C) for NO₂.

The effect of the red, green, and UV light illumination on sensor sensitivity was also investigated. Upon illumination, the conductance of the SnO₂/SWNTs hybrid nanostructures decreased due to photogenerated electron-hole pairs and by the removal of surface adsorbed oxygen molecules which reduces the density of the major p-type carriers in the SWNT-transducer. In general, the sensitivity, response and recovery times toward CO, NH₃, and NO₂ were improved. Moreover, the detection limit for CO was pushed down from 5 ppmv to 0.5 ppmv with the assistance of the UV illumination.
2.5 Reference

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(27) Nosang Vincent MYUNG; Syed MUBEEN; Ashok MULCHANDANI; Marc Arnold DESHUSSES; The Regents of the University of California: 2012; Vol. US 2012/0080319 A1.


Abstract:

Hybrid nanostructures of Pt nanoparticles functionalized single-walled carbon nanotubes (SWNTs) and Pt and SnO$_2$ co-functionalized SWNTs were synthesized on prefabricated microelectrodes by sequential electrochemical deposition process. The systematic study to obtain the optimum condition for Pt decorated SWNTs (Pt/SWNTS) and Pt decorated SnO$_2$/SWNTs (Pt/SnO$_2$/SWNTs) were performed and also correlate with its CO sensing performance. The optimum CO sensitivity of 0.04%/ppm of 50 ppm CO with the quick response (3.7 minutes) and recovery time (5.8 minutes) was achieved under room temperature with the Pt/SnO$_2$/SWNTs hybrid nanostructure. Light dependent sensing performance was examined with red, green and UV LED light under room temperature. With the assistance of the UV light illumination, the sensitivity of Pt/SnO$_2$/SWNTs was further enhanced to 2.1%/ppm to 50 ppm of CO and the detection limit can push down to 0.05 ppm.
3.1 Introduction

Carbon monoxide (CO) is a common by-product generated by incomplete combustion of carbon-containing materials. Common sources of CO include heating units, gas stoves, automobile exhaust gases, etc. Carbon monoxide intoxication is the most common type of fatal poisoning throughout the world including the United States\(^1\). Carbon monoxide can cause severe damage to the human heart and brain when the carboxyhemoglobin (COHb) levels in the blood exceed 20\(^\%\)\(^1\). This is because the affinity of hemoglobin for CO is 210 times higher than that for \(O_2\)\(^1,2\), resulting in hypoxia which may cause headache, nausea, loss of consciousness or even death. Moreover, CO becomes unstable and can become explosive when its volume percent concentration ranges between 12.50\(^\%\) and 74.20\(^\%\) in air\(^3\). In addition, its intrinsic properties of being colorless, odorless, tasteless and initially non-irritating make it very difficult to detect by conventional methods. Therefore, it’s crucial to develop new types of sensors that can detect CO below 50 ppm\(_v\) levels in the environment with high sensitive and rapid response.

The catalytic oxidation of CO to \(CO_2\) has long been a benchmark reaction in heterogeneous catalysts especially in many industrial processes, including the reduction of CO in automobile exhaust gases and the selective reduction in fuel cells\(^4\). During the past few decades, considerable efforts have been devoted to CO oxidation by noble metals in the form of single crystal or as nanoparticles in the supported metal oxides\(^5-8\). The influence of the metal particle sizes and density (on the support) have been intensively studied due to its significance from both fundamental and practical points of view\(^4\). The activity of the catalytic oxidation with varying metal particle size (1~10 nm) and density corresponds to
the available active sites, electronic states, interaction of metal and support, and oxidation states. The interaction of surface adsorbed oxygen and CO molecules is believed to be the main step in the oxidation process. There are two popular mechanisms to describe the entire oxidation process, the Langmuir-Hinselwood mechanism (L-H) and the Eley-Rideal mechanism (E-R). In the L-H mechanism, a CO molecule in the gas phase is first adsorbed onto the metal surface. Then it reacts with a surface adsorbed oxygen molecule to form the product CO₂, which is released to the air under the assumption of an isothermal steady state condition. In general, the CO oxidation on the Pt surface can for L-H mechanism can be simplified as equations 1-3.

\[
CO_{gas} \stackrel{k_1}{\rightarrow} CO_{ads} \quad (1)
\]

\[
O_2 \stackrel{k_3}{\rightarrow} 2O_{ads} \quad (2)
\]

\[
CO_{ads} + O_{ads} \stackrel{k_4}{\rightarrow} CO_2 \quad (3)
\]

In the E-R mechanism, a CO molecule in the gas phase reacts directly with a previously adsorbed oxygen molecule, without being adsorbed itself, to release the product CO₂ into the air. For the E-R mechanism the oxidation process can be expressed by the following equations 4-5.

\[
CO_{gas} + O_{ads} \stackrel{k_{ER1}}{\rightarrow} CO_{2gas} \quad (4)
\]

\[
CO_{ads} + O_{2gas} \stackrel{k_{ER2}}{\rightarrow} CO_{2gas} + O_{ads} \quad (5)
\]
The resulting rate law is typically complicated, where both mechanisms may be active. Although the exact sequence of events is not clear, the global reaction rate for both mechanisms is first order with respect to CO at atmospheric pressure\(^9\).

For the past few decades, a significant amount of effort has been put on CO oxidation and CO gas sensing. One dimensional (1-D) semiconductor metal oxide nanostructures have attracted great attention due to their promising applications in nanodevices. Various 1-D metal oxide nanostructures, such as nanobelts/nanowires/nanoribbons/nanofibers, have been used as transducers including ZnO\(^{13}\), SnO\(_2\)^{14-16}, MoO\(_3\)^{17}, and Ga\(_2\)O\(_3\)^{15,18} toward the detection of various analytes. Theses metal oxides demonstrated high sensitivity, fast response/recovery time, and low cost, which arises from their unique combination of redox chemistry, optical, electrical and semiconductor properties. Such good gas sensing performances have played a key role in the successful implementation of chemical sensor technology for many years. Despite of the exciting results reported on the gas sensing performance of metal oxides, the development of the ultra-sensitive, selective, and compact metal oxide based gas sensor for field use still remains a challenge. Nowadays, many efforts have been taken to enhance their sensitivity and selectivity, including heteroarchitectures\(^{19-21}\), functionalized with noble metal nanoparticles\(^{22-24}\), and/or under illumination\(^{25}\).

Noble metal nanocrystals have been found to play important roles in a number of chemical reactions, which range from solar water splitting\(^{26}\), CO oxidation\(^7\), gas sensing\(^{27-31}\) to photodecomposition of organic pollutants\(^{32}\). It has been known for a long time that transition metal composites with metal oxide support can enhance the CO oxidation
efficiency at elevated temperatures. There are various studies of CO oxidation on noble metal and metal oxide catalysts\cite{9}, and several explanations of these observation are given in the literature: (1) a bifunctional mechanism based on the spillover of both CO and O\textsubscript{2} from the noble metal to the metal oxide\cite{33}, (2) a bifunctional mechanism but only restrict on CO\cite{34}, (3) the CO oxidation existence on a new phase, a Pt-Sn alloy\cite{35}, (4) the promoting of the CO oxidation on the adjacent SnO\textsubscript{2} due to the adsorption of the reactants on the Pt surface\cite{9}, and (5) the spillover of the O\textsubscript{2} from the SnO\textsubscript{2} to the Pt surface\cite{9}. However, all the explanations mentioned above do not propose a way to minimize the CO poisoning effect at room temperature.

In this work, we fabricated both Pt/SWNTs and Pt/SnO\textsubscript{2}/SWNTs hybrid nanostructures for rapid CO sensing at room temperature. It should be mentioned that there are only a few CO sensors that can be operated at room temperature or near room temperature\cite{36}, but the sensitivity and selectivity is not competitive to the high temperature ones due to CO poisoning. To the best of our knowledge, we have demonstrated the first CO sensor that can detect CO down to 0.05 ppm at room temperature with the assistance of UV illumination.

3.2 Experimental Procedure

3.2.1 Electrode Microfabrication

Individually addressable sensor arrays consisting of 15 microelectrodes with 3 micron gaps were microfabricated onto a substrate using our previously developed photolithography\cite{31}. The substrate was a highly doped p-type Si wafer (Ultrasil Corporation, Hayward, CA) with a 300 nm oxidation layer deposited by low pressure
chemical vapor deposition. A positive photoresist AZ 5214-E (AZ Electronics Materials USA Corporation, Somerville, NJ) was spin-coated on the substrate at 1000 RPM for 2 s followed by 3000 RPM for 30 s then dried on a hot plate at 110°C for 5 minutes. The patterns were photolithographically defined by UV light at a 70 mJ/cm² exposure dose then immersed in a developer for 45 seconds (AZ 400K : DI water = 1 : 4, AZ Electronics Materials USA Corporation, Somerville, NJ). Gold film electrodes with a Ti adhesion under layer were e-beam deposited at 180 nm and 20 nm, respectively. The substrate was then soaked in acetone overnight for the lift-off process. Prior to experiments, these prefabricated microelectrodes were diced, cleaned with acetone and water, and blown dry with ultra-high purity N₂ gas.

3.2.2 SWNTs Alignment

SWNTs were aligned through AC dielectrophoretic alignment³⁷. Carboxylated-SWNTs (SWNT-COOH 80-90% purity, Carbon Solution, Inc., Riverside, CA, USA) were first dispersed (10 µg/mL) in N,N-dimethylforamide (DMF, Sigma Aldrich, MO, USA) and sonicated for 90 minutes at room temperature until a uniform suspension was obtained. The suspension was then transferred into a 50 mL Teflon centrifuge tube and centrifuged for 90 minutes at 15,000 RPM at 23 °C (Beckman J2-HS and JA-17 rotor, Beckman Coulter, Inc., Brea, CA, USA). After centrifuging, 10 mL of supernatant was immediately removed and put into a glass vial. The supernatant was then sonicated for an additional 60 minutes. Afterwards, 350 µL of the supernatant was placed into a customized Teflon cell with chip holder for SWNTs alignment. Optimal alignment was achieved in just 10 seconds after applying 2 Vpp at 4MHz to the electrodes. A Labview program was designed to
command the Keithley 3390 AC generator (aligner) and the custom-made DAQ switcher for sequential SWNTs alignment. The synthesized sensors were rinsed with DI water, dried with ultra pure N₂ gas and then calcined at 300 °C under a reducing environment (forming gas, 5% of hydrogen in nitrogen) for 1 hour to remove the residue from the solution and to improve the connection.

3.2.3 SWNTs Functionalization

3.2.3.1 SnO₂ Functionalized SWNTs Hybrid Nanostructures

The SnO₂/SWNTs hybrid nanostructures were obtained by functionalizing SWNTs with electrochemical deposition of tin dioxide from an electrolyte bath containing Sn²⁺. This electrolyte was prepared according to the previously published literature³⁸. 100 mM of sodium nitrate (≥ 99.0%, Sigma Aldrich, MO, USA) was added into 75 mM of nitric acid (70%, Sigma Aldrich, MO, USA) under constant stirring. 20 mM of tin chloride dehydrate (≥ 99.99%, Sigma Aldrich, MO, USA) was added with constant stirring for 12 hours prior to use. Finally, the pH of the solution was adjusted to 1.3 with HCl. LSV and chronoamperometry techniques were carried out at room temperature in the same customized Teflon cell with chip held [Figure 1(c)] by using a three electrode electrochemical setup. A commercial potentiostat/galvanostat (SP-200, Potentiostat/Galvanostat/EIS, BioLogic Science Instruments, France) was used for electrochemical deposition, where a Pt wire (99.99%, Sigma Aldrich, MO, USA) served as the counter electrode and a saturated Ag/AgCl electrode (CHI-111, CH Instrument, Inc., Austin, TX, USA) served as the reference electrode. For details regarding the optimization of the SnO₂ functionalized SWNTs hybrid process, reference our previous report³⁹.
3.2.3.2 Pt Functionalized SWNTs and Pt Decorated SnO$_2$/SWNTs Hybrid Nanostructures

The Pt decorated SnO$_2$/SWNTs hybrid nanostructures were obtained from two different concentrations of Pt electrode deposition precursor solution, 1 mM and 10 mM, respectively$^{40,41}$. LSV was utilized to characterize the electrochemical deposition of Pt. The ability to tune Pt particle size, particle density, and its morphology was demonstrated by controlling the applied potential and charge density. The deposition potential and charge density were optimized for CO sensing response.

3.2.4 Measurements and Material Characterization

The morphologies and compositions of the Pt/SWNTs and Pt nanoparticles decorated SnO$_2$/SWNTs hybrid nanostructures were investigated using field emission-scanning electron microscopy (FE-SEM, FEG-XL30, Philips) and energy-dispersive X-ray spectroscopy (EDS). The electrical resistance and electron transfer characteristics properties of these hybrid nanostructures were determined by two-probe measurements with a Keithley 236 source.

3.2.4.1 Gas sensing in the Absence of Light at Room Temperature

Furthermore, the sensing performance of the Pt/SWNTs and the Pt/SnO$_2$/SWNTs nanostructures were studied by installing the sensing chips in a customized sensing cell$^{39}$ (maximum three chips in three separate cells at one time) with inlet and outlet ports for gas flow and clipping them to a Keithley 236 source to obtain an electrical connection. The resistance was continuously recorded under an applied voltage fixed at 1 V. During the sensing measurement, the total gas flow rate was fixed at 200 sccm with desired analytes.
diluted with dry air. In all sensing experiments, sensors were first stabilized in dry air for 60 minutes, and then challenged with different concentrations of analytes with 15 minutes exposure and 20 minutes recovery times. The sensor response was determined by the resistance change before and after exposure to analyte and defined as \((R_f - R_o)/R_o\), where \(R_f\) is the final resistance of the peak height, and \(R_o\) is the initial baseline resistance prior to analyte exposure. The response time is defined as the time for the sensor to reach 90% of its steady-state value, and the recovery time is identified as the time required for the sensor after the exposure to return to 50% of its maximum response.

3.2.4.2 Gas Sensing in the Absence of Light at 100 °C

The sensing performance at 100 °C was carried out to understand the effect of the environment temperature and the relief of the CO poisoning effect. Before gas sensing, the entire sensing unit including Teflon cell and clip system was put in an oven (DVS 402, Yamato) for 30 minutes to stabilize the temperature. The sensing process was the same as mentioned above.

3.2.4.3 Light Dependent Gas Sensing Performance in the Presence of LED Light

In order to investigate the light dependent properties of the Pt/SWNTs and the Pt/SnO₂/SWNTs nanostructures, the red (\(\lambda=630\) nm, 7.2 mW, photon flux \(F = 1.44 \times 10^{14}\) /cm²s, LED630E), green (\(\lambda=525\) nm, 2.6 mW, photon flux \(F = 4.34 \times 10^{13}\) /cm²s, LED525E), and UV (\(\lambda=370\) nm, 2.5 mW, photon flux \(F = 2.98 \times 10^{13}\) /cm²s, LED370E) LED lights (Thorlabs, NJ, USA) were integrated into the customized sensing cell. The photocurrent was carried out at room temperature with the Keithley 236 source meter continuously recording under an applied voltage fixed at 1 V. For each LED light
photocurrent measurement, the light was on for 15 minutes exposure and off for 20 minutes recovery times for three cycles under the flow of dry air at 200 sccm. Furthermore, each LED light was on continuously through the entire sensing process.

3.3 Result and Discussion

3.3.1 Fabrication, Optimization and Characterization of Pt/SWNTs Hybrid Nanostructures

To understand the effect of electrodeposition parameters such as deposition potential and deposition charge density on the functionalization of SWNTs toward CO gas sensing performance, systematic study of Pt nanoparticles were carried out. First, the LSV was performed to achieve the deposition potential for Pt nanoparticles. The deposition potential was swept from +0.001 V of open circuit potential (OCP) to -1.0 V vs. a saturated Ag/AgCl reference electrode at a scan rate of 10 mV/s. In this work, saturated Ag/AgCl was selected as reference electrode in all experiments, if not mentioned specifically. Figure 6 shows a typical LSV of Pt deposition and transient curve on SWNTs. Three reduction waves (a₁, a₂ and a₃) were observed at -0.40, and -0.50 and -0.60 V, respectively. Equation 6 describes the Pt and its complex in equilibrium and the corresponding Nernst potential\textsuperscript{42,43}.

\[
P t C l_4^{2-} + 2e^- = P t + 4C l^- \quad E^o = 0.758 \text{ V vs. NHE} \tag{6}
\]

SEM images shown in Figure 2 demonstrate the SWNTs decorated with Pt nanoparticles under three deposition potential, -0.45, -0.55, and -0.625 V with three deposition charge densities, 0.00125, 0.0125, and 0.125 C/cm\textsuperscript{2}, respectively. From the observation of the SEM images, as a general rule, the Pt particle size increases while particle density decreases.
as the deposition charge density increases. This can be explained that when higher charge passed through, the Pt particles grow more uniformly and larger (spherical shaped) and they began to coalesce with adjacent particles, which results in less dense and round cluster shaped particles. The trend is shown in Figure 3, where the relation between the particle size and deposition charge density [Figure 3(a)] and the particle density and deposition charge density [Figure 3(b)] under three deposition potentials are plotted. Furthermore, as the charge density is increased to 0.125 C/cm$^2$, the morphology of the Pt nanoparticle changes from round to dendritic like shape. This could be possibly attributed to a large amount of Pt primary clusters were formed at the beginning, which grow larger when more negative cathodic deposition potential are applied. Those Pr clusters will combine with the adjacent clusters, leading to the dendritic like shape.
Figure 3.1 (a) Linear sweep voltammetry (LSV) of Pt deposition on SWNTs and (b) the corresponding transient curve at the potential of -0.45 (black), -0.55 (red) and -0.625 V (blue), respectively. Charge density: 0.00125 C/cm². Electrolyte: 1 mM of K₂PtCl₄, 10 mM of KCl. Total solution volume: 700 µL. LSV scan rate: 10 mV/s at room temperature.
Figure 3.2 SEM images of Pt/SWNTs hybrid nanostructures electrochemically deposited at different potentials and charge densities (a) potential: -0.45 V, charge density: 0.00125 C/cm², (b) potential: -0.45 V, charge density: 0.0125 C/cm², (c) potential: -0.45 V, charge density: 0.125 C/cm², (d) potential: -0.55 V, charge density: 0.00125 C/cm², (e) potential: -0.55 V, charge density: 0.0125 C/cm², (f) potential: -0.55 V, charge density: 0.125 C/cm², (g) potential: -0.625 V, charge density: 0.00125 C/cm², (h) potential: -0.625 V, charge density: 0.0125 C/cm², and (i) potential: -0.625 V, charge density: 0.125 C/cm², respectively.
3.3.2 Sensing Performance of Pt/SWNTs Hybrid Nanostructures at Room Temperature in the Absence of Light

3.3.2.1 Carbon Monoxide Sensing Performance

Figure 4 reveals the resistance change of the hybrid nanostructures after Pt electrochemical deposition under different charge densities and deposition potentials. As the Pt coverage increase, the resistance of the Pt/SWNTs hybrid nanostructures decreases. In particular, the resistance reduces to about 50% of the original value at the highest charge density. Figure 5 is the real time sensing toward CO of the Pt/SWNTs hybrid nanostructures fabricated under different conditions, and Figure 6 is the corresponding calibration curves. From Figure 5, the nine real time sensing plots could be divided into three sections. Section 1, with Figure 3 a, d, and g, all deposited at the same charge density of 0.00125 C/cm², but different deposition potentials of -0.45, -0.55 and -0.625 V, respectively; section 2, with Figure 3 b, e, and h, all deposited at the same charge density
of 0.125 C/cm², but also different deposition potentials of -0.45, -0.55 and -0.625 V, respectively; and section 3, with Figure 3 c, f, and i, deposited at the same charge density of 0.125 C/cm², and still different deposition potentials of -0.45, -0.55 and -0.625 V, respectively. Comparing the three sections, the optimum CO sensing response appears in section 2 where the Pt/SWNTs hybrid nanostructures synthesized with deposition potential of -0.625 V and charge density of 0.0125 C/cm², Figure 2h. This result is as expected since the particle density at this condition is the highest compared to those prepared under other conditions. A higher particle density can provide more active reaction sites for CO oxidation. It is worth noting that CO poisoning is present in all conditions, especially in sections 3, under the highest charge density. This is because the higher charge that passed through the SWNTs resulted in merging the Pt clusters into large particles with a diameter of around 200 nm; thus, decreasing their surface area relative to isolated islands of Pt clusters. The CO poisoning effect will be discussed in more detail later. The 3-D plot (Figure 7) clearly reveals the relationship between the resistance change and sensing performance. When the deposition charge density is 0.0125 C/cm². When deposited at the highest charge density of 0.125 C/cm², the hybrid nanostructures demonstrates the lowest sensing response, correlating to section 3 in Figure 5. When deposited at the lowest charge density of 0.00125 C/cm², the hybrid nanostructures demonstrated a medium sensing response, correlating to section 1 in Figure 5. When deposited at the charge density of 0.0125 C/cm², the hybrid structures demonstrated the highest sensing response, correlating to section 2 in Figure 5. In particular, at the deposition potential of -0.625 V, the CO sensing performance shows around 20% change in resistance. Therefore, the optimum condition
for CO sensing here is Pt/SWNTs deposited at the deposition potential of -0.625 V and charge density of the 0.0125 C/cm².

Figure 3.4 The resistance change after Pt nanoparticles deposition at varies charge densities with the deposition potential of -0.45 (black), -0.55 (red), and -0.625 (blue) V, respectively.
Figure 3.5 Real-time sensing performance of Pt/SWNTs hybrid nanostructures towards CO (a, b, c, d, e, f, g, h and i represent the responses acquired from hybrid structures of deposition condition shown in Figures 2 a, b, c, d, e, f, g, h and i, respectively).
Figure 3.6 Calibration curve for real-time sensing performance of Pt/SWNTs hybrid nanostructures towards CO [Deposition potential: (a) -0.45, (b) -0.55, and (c) -0.625 V, respectively].
Figure 3.7 Correlation of the Pt/SWNTs hybrid nanostructures sensing performance toward CO at deposition potential of -0.45, -0.55 and -0.625 V, respectively, and deposition charge density of 0.00125, 0.0125 and 0.125 C/cm², respectively. The optimum condition for CO sensing: deposition potential at -0.625 V and charge density at 0.0125 C/cm².
3.3.2.2 Carbon Monoxide Sensing Mechanism on Pt/SWNTs

CO sensing is part of a heterogeneous catalyst oxidation process; therefore, the concept of CO oxidation can be applied to explain the CO sensing performance. In this study, SWNTs work as support and transducer, converting the surface chemical reaction into the measurable electrical signal. It is believed that at low pressure (and ambient condition) conditions, CO oxidation take place through the Langmuir-Hinshelwood (L-H) reaction mechanism where oxidation process react within absorbed CO and oxygen. In this case, CO has been prooven to inhibit the adsorption of oxygen\(^6\,^{11}\). Thus, at low temperature, the CO oxidation rate increases as the CO desorption rate increases; in other words, minimal CO surface coverage. This phenomena has been reported in the literature\(^{44}\) showing a higher CO oxidation rate with an initial high O\(_2\) coverage. One particular phenomenon worth noting here is the CO poisoning effect on the CO oxidation process. This is because CO has a higher sticking probability than O\(_2\)\(^{44}\), and a lower O\(_2\) surface adsorption rate will lead to a lower CO oxidation rate. Therefore, for the CO heterogeneous catalyst oxidation process, (a) at low CO levels, the oxidation rate is proportional to CO concentration while (b) at high CO levels (> 0.5% in air), the rate becomes inversely proportional to CO. In conclusion, CO sensing performance can be enhanced by increasing the desorption rate of the CO molecules or creating the minimal CO coverage surface.

3.3.3 Fabrication, Optimization and Characterization of Pt Decorated SnO\(_2\)/SWNTs Hybrid Nanostructures

In our previous work\(^ {39}\), we systematically varied electrochemical paremeters to optimize SnO\(_2\)/SWNTs hybrid nanostructures toward CO sensing at room temperature.
Here, besides Pt decorated SWNTs, we also systematically investigate Pt decorated SnO$_2$/SWNTs hybrid nanostructures to further improve CO sensing performance at room temperature and minimize CO poisoning. Figures 8(a) and (b) show the same strand of a SnO$_2$/SWNTs hybrid nanostructure before and after Pt deposition from the 1 mM precursor solution. These images clearly exhibit the capability to selectively electrochemically deposit tin directly onto SWNTs. Figure 8(c) shows the Pt/SnO$_2$/SWNTs hybrid nanostructure after Pt deposition from the 10 mM Pt precursor solution. Particle size and density of the three configurations [Pt/SWNTs fabricated under optimum condition, Pt/SnO$_2$/SWNTs(1) obtained from the 1 mM Pt precursor solution, and Pt/SnO$_2$/SWNTs(10) fabricated from the 10 mM precursor solution] are shown in Table 1 for comparison.

The particle density of Pt/SWNTs [Figure 2(h)] is much larger than that of Pt/SnO$_2$/SWNTs(1) [Figure 8(b)] or Pt/SnO$_2$/SWNTs(10) [Figure 8(c)], because the lower current efficiency reduces the formation of Pt nuclei. Once the nuclei are formed, the grains grow rapidly, resulting in the formation of large Pt nanoparticles.

The resistances change before and after Pt deposition is shown in Figure 9(a). The I-V curve in Figure 9(b) reveals the conductivity change associated with the SEM images taken from the same sensor before and after Pt deposition. As expected, Pt nanoparticles deposited on SnO$_2$/SWNTs work as the scattering sites of the carriers, leading to the decrease of the conductivity. However, the conductivity of the Pt/SnO$_2$/SWNTs(10) nanostructures is slightly higher than that of Pt/SnO$_2$/SWNTs(1). This is due to the growth of the particle density and the particle size, which leads to the interconnection of Pt
nanoparticles and creates another carrier pathway; thus enhancing the conductivity slightly. The electron transfer characteristics are measured in ambient condition and plotted in Figure 10. Both Pt/SnO\textsubscript{2}/SWNTs(1) and Pt/SnO\textsubscript{2}/SWNTs(10) demonstrated p type semiconductor behavior as expected.
Figure 3.8 SEM images (a) of a single SnO$_2$/SWNT, (b) Pt nanoparticles deposited on SnO$_2$/SWNT from 1 mM Pt precursor solution (deposition potential of -0.625 V and charge density of 0.125 C/cm$^2$), and (c) Pt nanoparticles deposited on SnO$_2$/SWNTs from 10 mM Pt precursor solution (deposition potential at -0.625 V and charge density of 0.0125 C/cm$^2$), respectively.
Figure 3.9 (a) Resistance of SnO$_2$/SWNTs and Pt nanoparticles functionalized Pt/SnO$_2$/SWNTs, and (b) the I-V curves of SnO$_2$/SWNTs, Pt/SnO$_2$/SWNTs(1), and Pt/SnO$_2$/SWNTs(10), respectively. The solid symbols represent the resistance of SnO$_2$/SWNTs, and open symbols represent the resistance after the Pt nanoparticles deposition with different precursor solutions, respectively.
Figure 3.10 Electron transfer characteristics [Current (I_{SD}) vs. back gated voltage (V_G)] of Pt decorated SnO_2/SWNTs hybrid nanostructures obtained from 1 and 10 mM Pt precursor solutions, respectively.
Table 3.1 The particle size and density of Pt/SWNTs and Pt decorated SnO\textsubscript{2}/SWNTs from 1 mM and 10 mM Pt precursor solutions. The deposition charge density was fixed at 0.0125 C/cm\textsuperscript{2}.

<table>
<thead>
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<th>Pt/SnO\textsubscript{2}/SWNTs from 1 mM Pt solution</th>
<th>Pt/SnO\textsubscript{2}/SWNTs from 10 mM Pt solution</th>
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<td>Particle size (nm)</td>
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<td>Particle density</td>
<td>70.7 ± 3.8</td>
<td>20 ± 3.0</td>
<td>52.3 ± 2.1</td>
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</table>

3.3.4 Sensing Performance of Pt Decorated SnO\textsubscript{2}/SWNTs Hybrid Nanostructures at Room Temperature in the Absence of Light

3.3.4.1 Carbon Monoxide Sensing Performance at Room Temperature

In order to understand the sensing performance of Pt decorated SnO\textsubscript{2}/SWNTs, a preliminary CO sensing test was carried out for the concentrations of 50, 100, and 200 ppm, see Figure 11(a) for Pt/SnO\textsubscript{2}/SWNTs(1) and Figure 12(a) for Pt/SnO\textsubscript{2}/SWNTs(10), respectively. After that, we examined their sensing performance from 5 to 200 ppm of CO, and the corresponding data are shown in Figure 11(b) and Figure 12(b), respectively. Comparing the preliminary and full concentration sensing results of Pt/SnO\textsubscript{2}/SWNTs(1), the sensing responses towards both three-concentration [Figure 11(a)] and six-
The concentration of CO [Figure 11(b)] were improved for Pt/SnO$_2$/SWNTs(1) compared to Pt/SWNTs or SnO$_2$/SWNTs$^{39}$. For example, the resistance increased around 21% when exposed to 200 ppm CO [Figure 11(a)], compared to that of 15% [Figure 5h]. For Pt/SnO$_2$/SWNTs(10), the sensing performance was also improved, especially the response and recovery time was quite reduced, Figure 12(b). The opposite sensing pattern of the Pt/SnO$_2$/SWNTs(1) and Pt/SnO$_2$/SWNTs(10) indicates the typical p type and n type semiconductor sensing behavior for Pt/SnO$_2$/SWNTs(1) and Pt/SnO$_2$/SWNTs(10), respectively. It’s worth noting that CO poisoning is observed for both sensors, Figure 11(b) and Figure 12(b), where the sensing performance is negatively proportional to the increase of the CO concentration$^9$. Details are summarized in Table 3.2.
Figure 3.11 Real-time room temperature sensing performance of Pt/SnO$_2$/SWNTs(1) towards CO of (a) 50 to 200 ppm and (b) 5 to 200 ppm.
Figure 3.12 Real-time room temperature sensing performance of Pt/SnO$_2$/SWNTs(10) towards CO of (a) 50 to 200 ppm and (b) 5 to 200 ppm.
Table 3.2 Comparison of room temperature CO sensing properties of Pt/SWNTs and Pt/SnO$_2$/SWNTs hybrid nanostructures fabricated under optimum condition, respectively.

<table>
<thead>
<tr>
<th></th>
<th>Pt/SWNTs from deposition potential of -0.625 V</th>
<th>Pt/SnO$_2$/SWNTs in 1 mM Pt solution</th>
<th>Pt/SnO$_2$/SWNTs from 10 mM Pt solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO sensitivity (%/ppm)</td>
<td>0.05</td>
<td>0.14</td>
<td>0.04</td>
</tr>
<tr>
<td>Response time $t_{90}$ at 50 ppm (mins)</td>
<td>9.2</td>
<td>8.4</td>
<td>3.7</td>
</tr>
<tr>
<td>Recovery time $t_{50}$ at 50 ppm (mins)</td>
<td>16.2</td>
<td>13.5</td>
<td>5.8</td>
</tr>
</tbody>
</table>

3.3.4.2 CO Sensing Mechanism of Pt/SnO$_2$/SWNTs Hybrid Nanostructures

Various researchers have studied the oxidation of CO on either Pd/SnO$_2$ or Pt/SnO$_2$ catalysts, but there are very few reports using Pt/SnO$_2$/SWNTs as a CO gas sensor at room temperature. As mentioned in the introduction, there are five different hypotheses based on the observed CO on catalysts. Here, due to two different CO sensing patterns, the sensing mechanisms of Pt/SnO$_2$/SWNTs(1) and Pt/SnO$_2$/SWNTs(10) will be explained separately.
3.3.4.2.1 CO Sensing Mechanism on Pt/SnO$_2$/SWNTs(1) from the 1 mM Pt Precursor Solution

The CO sensing performance of Pt/SnO$_2$/SWNTs(1) can be explained if nearly all the CO is adsorbed on the Pt surface followed by the migration of CO to the Pt - SnO$_2$/SWNTs junction via surface diffusion. While the SnO$_2$ surface adsorbs O$_2$, O$_2^-$ and O', which diffuses to Pt and reacts with adsorbed CO via a L-H step releasing CO$_2$ as a product. One thing worth noting is that CO oxidation also exists on a Pt surface as described in the section of Pt/SWNTs hybrid nanostructures, section 3.3.2. However, owing to the higher sticking coefficient of CO than O$_2$, CO obstructs the O$_2$ adsorption on Pt, which consequently inhibits CO oxidation and causes CO poisoning.

After reaction, the electrons are released back into the hybrid nanostructures, leading to the recombination of electrons and holes. This results in decreasing the conductivity. Thus, the resistance increases during CO sensing progress. The hypothesis mentioned above have been verified by the simulation via Monte Carlo methods$^9$ with 4 wt% Pt loading on SnO$_2$. In the simulation, with solely Pt and/or Pt/SnO$_2$, the oxidation process is negatively proportional to the CO concentration in line with our sensing performance.

3.3.4.2.2 CO Sensing Mechanism on Pt/SnO$_2$/SWNTs from the 10 mM Pt Precursor Solution [Pt/SnO$_2$/SWNTs(10)]

Although the electron transfer characteristics of Pt/SnO$_2$/SWNTs(10) show a weak p-type semiconducting behavior (Figure 10), the CO sensing performance in Figure 12 indicates a n-type semiconducting sensing mechanism. This might be due to the increase
in the Pt particle density resulting in the larger surface active sites. Since CO mainly adsorbs on the Pt surface, the increase in particle density (from 20 to 50 particles/SWNT) with similar particle size, generates more surface area for CO oxidation, which improves the response time, Figure 12. The increase in the particle density also creates the chance for the Pt clusters to connect with each other and provides another electron pathway. After CO oxidation, the released electrons flow into the Pt clusters instead of flowing back to the hybrid nanostructures causing the separation of the electrons and holes. Consequently, the separated holes move back to the SWNTs and increase the conductivity.

3.3.4.3 CO Sensing at Elevated Temperature

The oxidation efficiency of CO on a surface increases with surface temperature and reaches a maximum efficiency around 170 °C\textsuperscript{45,46}. It is believed that the adsorption of CO is strongly favored at room temperature, but it gradually diminishes as the temperature increases\textsuperscript{47}. In another words, the CO surface coverage is inversely proportional to temperature\textsuperscript{48}. This effect is consistent with other metal/SnO\textsubscript{2} hybrid nanostructures sensing CO at 100 °C\textsuperscript{36}. Figure 13 shows the real time CO sensing performance of our Pt/SnO\textsubscript{2}/SWNTs hybrid nanostructures at 100 °C. For the case of Pt/SnO\textsubscript{2}/SWNTs(1), although the response decreases (i.e., 3% for 50 ppm CO compared to 13% for 50 ppm at room temperature), CO poisoning is suppressed. This expected result is owing to the enhancement rate of CO desorption and CO migration on a Pt surface.

In the case of Pt/SnO\textsubscript{2}/SWNTs(10), the CO poisoning was also reduced and it showed a p-type semiconducting behavior which is opposite to the sensing pattern at room
temperature. This might be attributed to the change of surface chemistry at elevated temperature.

Pt/SWNTs were also tested at 100 °C, but the sensing performance was not enhanced as much as Pt/SnO$_2$/SWNTs (data not shown here).

**Figure 3.13** Real-time CO sensing performance at 100 °C for Pt/SnO$_2$/SWNTs hybrid nanostructures (from 1 mM and 10 mM Pt precursor solutions, respectively) and their calibration curve.

3.3.5 Sensing Performance of Pt Decorated SnO$_2$/SWNTs Hybrid Nanostructures under the Illumination of LED Lights

3.3.5.1 Photocurrent Measurement

Although the CO poisoning effect can be reduced at elevated temperatures, an undesirable side effect at elevated temperatures is a large reduction in the chemiresistive response. To optimize both, we systematically investigated the sensing response of the Pt/SnO$_2$/SWNTs hybrid nanostructures to CO back at room temperature but under the assistance of continuous illumination from three different LED light sources; namely, red (2 eV photons @) $1.44 \times 10^{14}$ /cm$^2$s), green (2.36 eV photons @ $4.34 \times 10^{13}$ /cm$^2$s $)$, and UV
(3.35 eV photons @ 2.98×10^{13} /cm²s) lights. Figure 14 shows the typical, discrete drops in photocurrent (and their slow recovery rates) for both (a) the 1mM and (b) the 10 mM Pt solutions as the photon energy of the illumination source increases from red to green to UV light, and where ΔI/I₀ is defined as the difference between the illuminated and dark current values divided by the dark current. There are two processes that are occurring in the metal oxide upon LED illumination. Firstly, photons (such as 3.35 eV UV photons) whose energy exceed the band gap energy of SnO₂ (E₉ = 3.2 - 3.6 eV) can photogenerate electron-hole pairs⁴⁹ (Equation 7). Secondly, the surface adsorbed oxygen molecules are photodesorbed upon the exposure of light (Equation 8)⁴⁹,⁵⁰. After the light is turned off, the desorbed oxygen molecules will re-adsorb onto the SnO₂ surface and withdraw electrons from the hybrid nanostructures, resulting in an increase in their conductivity (Equation 9).

\[ hν \rightarrow e^- + h^+ \]  
(Eq.7)
\[ O_2^-(ad) + h^+ \rightarrow O_2 (g) \]  
(Eq.8)
\[ O_2(g) + e^- \rightarrow O_2^- (ad) \]  
(Eq.9)

In the case of Pt/SnO₂/SWNTs(1), under the red (~ 2eV) light, the photon energy is much lower than the band gap energy of SnO₂ (3.6 eV); therefore, there is no photocurrent change. For green light (~ 2.36 eV) and UV light (~ 3.35 eV), the photon energy is near or higher than the band gap energy of SnO₂, which means they can excite electron-hole pairs and induce the observed 5% decrease in the current.

In the case of Pt/SnO₂/SWNTs(10), there was a 5% change in photocurrent under red light illumination but a more significant change occurred under green (15%) and UV light (22%) illuminations. This might be due to the effect of localized surface plasmon
resonance (LSPR). Two mechanisms are possibly involved; namely, plasmonic enhancement of the light adsorption and plasmonic sensitization. Upon illumination, the incident photons excite the LSPR in the noble metal nanocrystals and generate electron-hole pairs in the semiconductor simultaneously. The part of the semiconductor that is adjacent to the metal nanoparticle is equivalent to being put into a strong local electric field whose intensity is several orders of magnitude higher than the incident light. Due to the high density of Pt nanoparticles in Pt/SnO$_2$/SWNTs, this locally enhanced electric field promotes the generation rate of electron-hole pairs. In addition, under the resonant excitation of the metal nanoparticles, a population of extra thermal electrons is generated. Those electrons within this population whose energy are higher than the Schottky barrier can inject themselves into the SnO$_2$ conduction band. The excess electrons then flow into the SWNTs and recombine with the holes, thus, decreasing the nanotube’s conductivity.
Figure 3.14 Photocurrent sensing response of (a) Pt/SnO$_2$/SWNTs(1) and (b) Pt/SnO$_2$/SWNTs(10) under the illumination of red (red), green (green), and UV (violet) light, respectively.

3.3.5.2 CO Sensing under the Illumination of LED Light and Sensing Mechanisms

Figure 15 demonstrates the CO sensing under the illumination of red, green and UV light from 5 to 200 ppm in ambient condition for the Pt/SnO$_2$/SWNTs hybrid nanostructures. Figure 15(a) displays the CO sensing performance of Pt/SnO$_2$/SWNTs(1) in the absence of light, under red, green, and UV light, respectively. There are three points worth noting. First, under the radiance of red light, the adsorption energy for CO on Pt (126-176 kJ/mol)$^{53,54}$ falls in the range of the red light. Therefore, CO adsorption is inhibited and results in the continuous increase of the resistance. Second, under the illumination of the green and UV light, the Pt nanoparticles work as the amplifiers (LSPR effect) for the incident light to enhance the generation of the electron-hole pairs. The electrons were captured by CO molecules to form some surface adsorbed molecules, which continue to oxidize CO by the L-H mechanism. At the same time, the electron holes flow into the SWNTs, this increases the hybrid nanostructure’s conductivity. Under this circumstance,
the conductivity of entire hybrid nanostructure increased upon CO exposure. The last point is that the dynamic range of CO sensing is narrow under the assistance of light illumination. The CO sensing mechanism of Pt/SnO$_2$/SWNTs(10) under light illumination is the same as that of Pt/SnO$_2$/SWNTs(1) nanostructures. The sensing performance and dynamic range are further improved [Figure 15(b)] because of the higher density of the Pt nanoparticles which enhanced the generation of electron-hole pairs. Figure 16 shows that with the assistance of UV light, the detection limit of these Pt/SnO$_2$/SWNTs(10) hybrid nanostructures towards CO is down to 0.05 ppmv, which is the lowest for room temperature CO sensors so far.
Figure 3.15 Room temperature CO sensing of (a) Pt/SnO$_2$/SWNTs(1) and (b) Pt/SnO$_2$/SWNTs(10), respectively. [No illumination (black open square), under the illumination of red (red), green (green) and UV light (violet), respectively.]

3.3.5.3 NH$_3$ and NO$_2$ Sensing under the Illumination of LED Light

The sensors are also challenged with background analytes such as NH$_3$ and NO$_2$ to identify the potential interference and demonstrate the sensor viability in the practical application. Figures 17 and 18 show the sensing performance of Pt/SWNTs and Pt/SnO$_2$/SWNTs with and without light illumination. In general, the sensitivity, response and recovery time were promoted under light illumination. Morphology-dependent sensing performance was observed for Pt/SnO$_2$/SWNTs especially for the case of NH$_3$ (Figure 17). In this case, the
response doubled compared to the one sensing in the absence of light, which is consistent with previously published results\textsuperscript{55}. Overall, the presence of the Pt nanoparticles boosts the adsorption of NH\textsubscript{3} and enhances the sensing performance. This phenomena could be amplified under the illumination of UV light owing to the generation of extra electron-hole pairs speeding up the surface reaction for NH\textsubscript{3}\textsuperscript{56}.

For the case of NO\textsubscript{2} sensing under UV light illumination (Figure 18), the response and recovery time were improved. This is because the electron holes from photo-generated electron-hole pairs recombine with NO\textsubscript{2} and will be adsorbed on the surface under the UV light\textsuperscript{56,57}.

3.4 Conclusions

CO gas sensors displaying high sensitivity were demonstrated using transducer elements operated at room temperature made of SWNTs based hetero-nanostructures. In particular, a sequential electrochemical deposition approach was used to functionalize SWNTs with Pt, with SnO\textsubscript{2}, and co-functionalized with SnO\textsubscript{2} followed by Pt nanoparticles. Shape, size and morphology of the Pt particles were controlled by adjusting the electrodeposition potential, doposition charge density, and electrolyte composition. The deposition of Pt on SWNTs yielding Pt/SWNTs followed the stages of classical nucleation and growth starting with nucleation of small Pt particles along the SWNTs followed by the growth of these nuclei into small Pt clusters and finally growing into highly crystalline Pt round structures. Dendritic Pt structures were observed when the deposition potential (driving force) was increased from -0.45 V to -0.625 V – apparently enhancing instability in the spherical morphology giving way to preferred growth directions. The density of the
Pt nanoparticles in the Pt/SnO₂/SWNTs hybrid nanostructure was controlled by the concentration of the Pt precursor solution (1 and 10 mM solutions from K₂PtCl₄).

The Pt functionalized SWNTs, especially the Pt/SnO₂/SWNTs hybrid nanostructures, operating at room temperature displayed an enhanced sensitivity toward CO. The Pt/SWNTs hybrid, fabricated at a charge density of 0.0125 C/cm² and a deposition potential of -0.625 V, displayed a 10% resistance changing when exposed to 50 ppm of CO, whereas the Pt/SnO₂/SWNTs nanostructure demonstrated a shorter response time (9.2 to 3.7 minutes) and recovery time (16.2 to 3.8 minutes) under the same exposure. The enhancement in the sensing performance observed for Pt/SnO₂/SWNTs hybrid nanostructures is attributed to the Pt nanoparticles, which serve as catalytic activators for CO oxidation. Additionally, with the assistance of UV illumination, the CO poisoning effect was eliminated and the room temperature limit of detection was lowered to 0.05 ppm [Pt/SnO₂/SWNTs(10)]. The sensors were also tested against background analytes to demonstrate viability in the field.
3.5 Reference


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4 Metal Nanoparticles and DNA Co-Functionalized Single Walled Carbon Nanotubes Gas Sensors

Abstract:

Metal/DNA/SWNTs hybrid nanostructures based gas sensor array were fabricated by means of ink jet printing of metal ions chelated DNA/SWNTs on microfabricated electrodes, followed by electroless deposition to reduce metal ions to metal. DNA served as a dispersing agent to effectively solubilize pristine SWNTs in water and as metal ion chelating centers for the formation of nanoparticles. Noble metals including palladium, platinum, and gold were used because the high binding affinity towards specific analytes thus to enhance the selectivity and sensitivity. The sensitivity and selectivity of the gas sensors toward various gases such as H₂, H₂S, NH₃, and NO₂ was determined at room temperature. Sensing results indicated the enhancement of the sensitivity and selectivity toward certain analytes by functionalized with different metal nanoparticles (e.g., Pd/DNA/SWNTs for H₂ and H₂S). The combined responses give a unique pattern or signature for each analytes by which the system can identify and quantify an individual gas.
4.1 Introduction

Electronic noses (E-nose) which simulated the human olfactory was advanced as a promising device to accurately identify, differentiate, and quantify the presence of hazardous gaseous chemicals to improve the quality of lives\cite{1}. Over the years, several sensor configurations have been developed by detecting different changes of transducers’ properties ranging from piezoelectric\cite{2} which monitoring the frequency change of functionalized polymers coated electrodes when absorb gaseous molecules to chemiresistive/conductometric sensors that generate the electrical resistance/conductance change upon gas adsorption/reaction on semiconducting sensing materials\cite{3}. Compare to other sensor modes, chemiresistive metal oxide sensors drew researcher’s attention because of the robust nature, simple circuit design, and low-cost for miniaturized and field deployable device. Despite of good sensitivity, fast response/recovery time, and long-life time, metal oxide based chemiresistors need to operate at high temperature which ultimately increased the power consumption. On the other hand, short-life time, drift of the resistance, and greater inference from humidity overshadow the advantages of conducting polymers based chemiresistors such as room temperature operation, good response to a wide range of analytes, and fast response/recovery time to polar gaseous compounds\cite{4}. Consequently, facile approaches, which provide considerable benefits in terms of low cost and manufacturability for mass production, to synthesize rapid response, reversible and selective gaseous chemical detection sensor array at room temperature, are essential for environmental monitoring.
Advancement in nanotechnology have prompted the utilization of one-dimensional (1-D) semiconducting nanostructures as novel sensing and/or transducer materials due to their ultra-high surface area to volume ratio that enhances surface adsorptive capacity, tunable electrical properties via dopants which later control the sensing performance, and the ability to form ultra-high density array in small dimensions. In particular, single walled carbon nanotubes (SWNTs) are a promising 1-D nanomaterial due to their excellent electronic properties, and thermal and chemical stability under room temperature to develop devices with miniaturized size, simplicity, reliability, and low cost [5-8]. The unique properties of SWNTs have motivated researchers to advance on the SWNTs based chemical sensor. Among them, SWNTs based chemiresistor has been widely applied due to their sensitivity toward various gaseous analytes via charge interaction and simple measurement set up. Pristine SWNTs shows remarkable adsorptive ability due to large surface area and once interact with NH$_3$, NO$_2$ and aromatic compounds, the electric behavior changed depend on the exposing analytes; nevertheless, as a sensing material, pristine SWNTs have drawbacks specifically on low sensitivity, lack of selectivity and long recovery which hinder its use to make a applicable gas sensor[9]. Numerous efforts have been devoted to surface functionalization of SWNTs, covalently or noncovalently, to improve their sensing performance including sensitivity and selectivity[9]. Current progresses have shown that sensitivity toward certain analytes further enhanced by introducing functional groups[10, 11]. Numerous synthetic routes have been reported for the preparation of functionalized SWNTs; each provided varies degree of controlling the size and distribution of the decorated SWNTs. These approaches can be divided into three
general categories: 1) electrochemical and chemical processes[12, 13], 2) dispersion of nanoparticles on the surface of SWNTs [14], and 3) physical deposition including sputtering and e-beam evaporation[15]. Although a large variety of the metal nanoparticles decorated carbon nanotubes have been successfully synthesized via physical routes, expensive equipment and high power consumption are the major concern and disadvantages. Homogeneous, highly stable and highly concentrated dispersed SWNTs with similar particle size distributions could be achieved from dispersion of nanoparticles. However, special functionalization steps of SWNTs are needed, e.g., chemically functionalize SWNTs with thiol group (–SH)[14] to react with gold. Moreover, extra purification steps are needed, which resulted lower yield for the final SWNTs.

Electrochemical process is a powerful technique to deposit wide range of metal/metal oxide on the surface of the SWNTs due to the capability to control size and composition tuning. These hybrid nanostructures has been demonstrated the capability of enhance the selectivity and sensitivity toward specific target analytes such as Pt[15, 16] and Pd for H₂[13], Au for H₂S[17] and elemental mercury vapor[18], and ZnO and SnO₂ for H₂S, Xylene and VOCs[11, 19]. Instead of decorating inorganic compounds, conducting polymer, e.g., PEDOT-PSS or polyaniline (PANI), and polythiophene[20, 21], via chemical or electrochemical processes functionalized to the surface of SWNT has shown great sensing performance.

Despite the remarkable electrical and mechanical properties SWNT possesses, poor solubility in aqueous and non-aqueous solution cause a considerable challenge in many
applications require uniform dispersion such as field effect transistor and chemical and biological manipulation in fundamental and practical research fields. Functionalized SWNTs with various functional groups such as carboxylic and PABS groups was realized to enhance the solubility of SWNTs as well as introduce the structural defect sites, destroying intrinsic mechanical and electrical properties of intrinsic SWNTs. In order to maintain the intrinsic electrical properties as well as the structural configuration, surfactants were introduced via noncovalently decorating in the solution to disperse carbon nanotubes into smaller bundles or individual tube. Pristine SWNT has been successfully solubilized in aqueous media by adsorption of sodium dodecyl sulfate (SDS)[22], sodium cholate[23], sodium dodecylbenzene sulfonate (SDBS)[24], and polymer rapping[25]. In particular, Deoxyribonucleic acid (DNA) revealed better dispersion efficiency compare to other polymers been used[26]. This is owing to the π stacking interaction which overcomes the van der Waals attraction energy of 500 ev/µm[27] between each carbon nanotube resulting separation from the large bundles[28]. Besides, DNA, a readily available biopolymer, is an excellent chelating/complexing for nanostructures because its rich chemical functionality allows it to interact with a variety of nanomaterials of interest. For decades, deposition of cobalt[12], copper[29], gold[30], nickel[12], palladium[31], platinum[32], and silver[33] on DNA has been investigated and successfully fabricated. To the best of our knowledge, the metal nanoparticles decorated DNA/SWNTs hybrid structures (Pt/DNA/SWNTs) were synthesized but not for the purpose of gas sensing[34, 35].
In this work, a series of metal/DNA/SWNTs based hybrid nanostructures sensor arrays were fabricated by an ink jet printing to pattern metal ions (e.g. Au, Pt, and Pd) chelated DNA/SWNTs onto pre-fabricated microelectrodes followed by electroless reduction to form metal nanoparticles (NPs). DNA was selected because its ability to serve both as dispersion and chelating agents. Ink jet printing was used to deliver metal ions chelated DNA/SWNTs to prefabricated electrodes because its (1) ability of purely additive on top of the existing features or patterns that where are needed, (2) flexibility of choosing structure design by simplify changing the software based printer control system, (3) ability to pattern the organic materials such as biological materials (DNA/RNA or proteins) that are not compatible with conventional photolithography alignment process, (4) compatibility for bulk/wafer scale printing with high repeatability, (5) low cost[36]. The ability to tune the SWNTs gas sensing performance, including sensitivity and selectivity were demonstrated through control over the ratio of DNA and SWNTs and different metals deposition to form hybrid nanostructures. These decorated hybrid nanostructures devices were exposed towards four different gases: H₂S, H₂, NH₃, and NO₂, respectively. Sensing performance of these hybrid nanosensors in terms of sensitivity, selectivity, as well as response and recovery time was correlated to the metal decorated on the hybrid nanostructures.
4.2 Experimental Procedure

The individually addressable sensor array consists of 24 microelectrodes with 3 micron gap were microfabricated using photolithography (Figure 1). Thermally oxidized highly doped p-type Si wafer (Ultrasil Corporation, Hayward, CA) with 300 nm oxidation layer (grown by Low Pressure Chemical Vapor Deposition) was used as the substrate. First, a positive photoresist AZ 5214-E (AZ Electronics Materials USA Corporation, Somerville, NJ) was spin-coated on the substrate at a speed of 1000 RPM for 2 s followed by 3000 RPM for 30s, and then the substrate was placed on a hot plate at 110°C for 5 min. The patterns were photolithographically defined onto the substrates by being exposed under UV with a 70 mJ/cm² exposure dose and subsequently developed by immersing it into a developer (AZ 400K : DI water = 1 : 4, AZ Electronics Materials USA Corporation, Somerville, NJ) for 45 seconds. Afterwards, Ti (an adhesion layer) and Au films were e-beam deposited with the film thickness of 20 nm and 180 nm, respectively. The substrate was soaked into an acetone bath overnight for lift-off process. Prior to experiments, these prefabricated microelectrodes were diced, cleaned with acetone and water, and blow dried with ultra high purity N₂ gas for further uses.
Figure 4.1 Optical images of (a) patterned electrodes on a silicon wafer, (b) electrodes array with 3 micron single gap.

Figure 2 illustrates the experimental steps to fabricated Metal/DNA/SWNTs based gas sensors. Carbon nanotube suspension inks were prepared by mixing commercially available as-prepared SWNTs (AP-SWNT, Caron solution Inc., Riverside, CA) and sodium salt salmon testes DNA (% G-C content = 41.2%, MW = $1.3 \times 10^6$ approximately 2000 bp from Sigma) in 1:1 ratio. Salmon DNA was selected throughout this work because it is relatively inexpensive, stable, and easy to obtain in large quantities. The resulting DNA/SWNTs solution was sonicated for 90 minutes (temperature was maintained at 9°C or less) until a uniform suspension was obtained. Then the suspension was centrifuged at 13,200 RPM for 15 minutes and the supernatant was subsequently collected. The concentration of the SWNTs was determined by a UV-Vis Spectrophotometer (Beckman Coulter Model DU®800) using a calibration curve at the wavelength of 730 nm and the calculated concentration is independent of the solution’s pH[37]. Afterwards, metal ion chelated DNA wrapped SWNTs inks were made by mixing DNA/SWNTs ink and 1 mM
of corresponding metal ion solution. In this work, palladium chloride (PdCl₂, pH = 5, incubation time of 6 hours) for Pd, potassium tetrachloroplatinate (K₂PtCl₄, pH = 5, incubation time of 8 hours) for Pt, and chloroauric acid (HAuCl₄, pH = 5.3, incubation time of 6 hours) for Au were used to synthesize metal ion chelated DNA/SWNTs hybrid structure. Finally, the resulting mixtures were desalted by dialysis through semipermeable membrane (molecular weight cut off 12-14 kD, SpectroPor®) against nanopure water for overnight.
Prior to ink jet printing process, the prefabricated microelectrodes were cleaned with oxygen plasma at 200 Watts for 2 min (Oxford Plasmalab 100/180) under the pressure of 20 mTorr and then placed on the plate of Fujifilm Dimatix DMP 2831 piezoelectric ink jet printer. The dialyzed ink was filled into 1 mL cartridge and inserted to the printer. Different jetting voltage and frequency conditions were tested. As shown in Figure 3, one droplet
instead of multiple droplets was achieved by applying a voltage of 15 V at 10 KHz, which shows perfect round shape without droplet tail and the jetting directing was straight to the substrate. Dot patterns were printed onto the prefabricated microelectrodes from silicon based nozzles at the applied voltage of 15 V and frequency of 10 kHz according to the preliminary result. The printing cycle was set up for 20 times to reach the required resistance range, and the clean cycle was fixed for every 5 prints to avoid clog and miss alignment. Metal/DNA/SWNTs hybrid nanostructures were finally obtained by dipping the substrate into 2 mL of aqueous electrolyte containing 2.5 g/L of dimethylamino borane (DMAB) solution, 25 g/L of sodium citrate, and 25 g/L of 85% lactic acid; the pH was adjusted to 7.4 with NH₄OH[31]. After 4 minutes, the microelectrodes were gently rinsed with nanopure water and blow dried with ultra-purity nitrogen gas.
Figure 4.3 Droplet images for default wave form. Satisfactory droplet was obtained at applied voltage 15 V and frequency of 10 kHz.

The morphologies and compositions of the metal/DNA/SWNTs hybrid nanostructures were investigated using field emission-scanning electron microscopy (FE-SEM, FEG-XL30, Philips), transmission electron microscopy (TEM, FEI-PHILIPS CM300) and energy-dispersive X-ray spectroscopy (EDS). The electrical resistances of these hybrid nanostructures were determined by two points measurement with a Keithley 236 source measurement. Furthermore, the sensing performance of the metal/DNA/SWNTs hybrid nanostructures was studied by installing the sensing chip in a sealed homemade glass dome with gas inlet and outlet ports for gas flow and then clipping the chip to a Keithley 236 source measurement to obtain electrical connection [Figure 2 (c)]. The applied voltage was
fixed at 1 V where the resistance was continuously recorded. During the sensing measurement, the total gas flow rate was fixed at 200 sccm and dry air was used as the carrier gas in all the experiments. Finally, the configuration of the sensing system was designed to measure each sensor in series simultaneously with multiplexers.

4.3 Results and Discussion

4.3.1 DNA/SWNTs Ink Preparation

The presence of DNA promoted the dispersion of as-prepared SWNTs in nanopure water [Figures 4 (a) and (b)] and the supernatant of DNA/SWNTs [Figure 4 (c)] remained stable for one week. The dispersion ability of as-prepared SWNTs increases with increasing DNA concentration. As shown in Figure 4 (d), solubilize SWNTs concentration increased from 0.13 mg/mL and 0.16 mg/mL when the ratio of DNA:SWNTs increased from 1:1 (w/w) and 10:1 (w/w), respectively. When the ratio of DNA:SWNTs is fixed at 100:1 (w/w), the soluble SWNTs concentration can reach upto 0.23 mg/mL which is approximately 85% of the starting SWNTs. However, as the ratio of DNA:SWNTs increases, the excess DNA segments can provide more metal chelation sites preventing metal ions binding to the DNA/SWNTs hybrid nanostructures. Therefore, as-prepared SWNTs are dispersed with equivalent weight of DNA in this work.
Figure 4.4 Optical images of (a) as-prepared SWNTs ink, (b) DNA/SWNTs ink and (c) supernatant from (b), and (d) concentration of soluble SWNTs plotted as a function of salmon taste DNA concentration measured by UV-Vis at the wavelength of 700 nm.

4.3.2 Ink-jet Printing of DNA/SWNTs Inks

Upon ink-jet printing of DNA/SWNTs, the challenge comes from the coffee ring effect, which prohibits the uniform distribution of the SWNTs. This phenomenon is due to inhomogeneous, uneven evaporation of a liquid. During the drying step, attractive capillary forces facilitated particles aggregation towards the rim of the droplet, resulting in a dense,
ring-like deposition on the flat surface[38]. However, the formation of coffee ring effect is still in debate. Unlike what Deegan et al. recommended that contact line of a droplet pinned causing replenishing flow from the centre, Sommer et al.,[39] indicated that this phenomenon is independent to the pinning of droplet contact line. While Hu and Larson[12] suggested that formation of coffee ring deposition requires not only a pinned contact line but also a suppression of Marangoni flow. Although there is no cure for all solution to reduce or eliminate the coffee ring effect, several approaches have been proposed. Printing on the heated substrate can minimize the formation of coffee ring deposition in some systems due to the enhancement of solvent evaporation rate reducing material transfer to contact line. In this work, coffee ring effect is more pronounced as substrate temperature increased and multiple rims formed. The use of binary mixture of solvents demonstrate uniformly printed pattern when one solvent with higher boiling point. Coffee stain shrinks due to the increasing percentage of higher boiling point solvent near the pinned contact line resulting slower evaporation rate and diminishing the outward convective flow[40]. Surface treatment of substrate provides the alternative route to reduce the coffee stain deposition. Small et al.[6] reported that as substrate hydrophobicity increases so as the formation of coffee ring. Oxygen plasma treated of SiO$_2$ surface exhibits higher degree of hydropilicity resulting uniform distribution of carbon nanotubes network[11]. In this work, we used oxygen plasma treatment technique to enhance the hydrophilicity to minimize the coffee ring effect. Figures 5 (a) and (b) show the contact angles of the silicon dioxide before and after oxygen plasma treatment which were 40.5° and 17.3°, respectively. As expected, the DNA/SWNTs network dispersed better on the
more hydrophilic surface while thick and aggregated ring structure of a dried droplet can be clearly seen on the untreated more hydrophobic SiO$_2$ chip [Figures 5 (c) and (d)].

**Figure 4.5** (a) Untreated SiO$_2$ chip with the contact angle of 40.5°, (b) oxygen plasma treated SiO$_2$ chip (200 Watts, 2 min) with the contact angle of 17.3°, and (c) and (d) are the SEM images of (a) and (b) after drying under room temperature, respectively.
4.3.3 Metal/DNA/SWNTs Hybrid Nanostructures Fabrication

During the incubation in electrolyte containing metal ions, metal ions attached to DNA forming complex structures, and act as efficient nucleation sites for the growth of the nano-crystalline particles[32]. The SEM observation of DNA/SWNTs network (Figure 6) shows that DNA formed clusters instead of wrapping up SWNTs. After incubation, the dialyzed solution was printed via the piezoelectric ink jet printer on to the pretreated chip and dip into the dimethylaminoborane (DMAB) solution for electrochemical reduction of chelated metal ions. DMAB was selected as the reducing agents because its stability in electroless deposition bath with wild range of pH and temperature without self-decomposition[41]. The standard redox potential for Au, Pt, Pd and DMAB (Eq. 1-4) are listed below where the oxidation of DMAB provides three electrons to reduce the metal ion complexes bound on DNA to form metal. [32, 42].

\[
\text{AuCl}_4^{-}(aq) + 3e^- \rightarrow \text{Au}(s) + 4\text{Cl}^-_{(aq)} E^o = 1.00 \text{ V vs NHE} \\
\text{(Eq.1)}
\]

\[
[\text{PtCl}_4]_{2(aq)}^- + 2e^- \rightarrow \text{Pt}(s) + 4\text{Cl}^-_{(aq)} E^o = 0.76 \text{ V vs NHE} \\
\text{(Eq.2)}
\]

\[
Pd_{(aq)}^{2+} + 2e^- \rightarrow Pd_{(s)} \quad E^o = 0.92 \text{ V vs NHE} \\
\text{(Eq.3)}
\]

\[
(CH_3)_2NHBH_3 + 4OH^- \rightarrow BO_2^- + \frac{3}{2}H_2 + 2H_2O + (CH_3)_2NH + 3e^- \quad E^o = -1.18 \text{ V vs NHE} \quad \text{(Eq. 4)}
\]

Figures 6 (a-c) show TEM images of the metal/DNA/SWNTs [Au (a), Pt (b), and Pd (c)] nanostructures after electroless deposition and Figure 7 (d) shows the average particle sizes of metal nanoparticles. In TEM images, the long hollow tubes are SWNTs, and the black spherical particles on top of them are the decorated nanoparticles, which show similar
morphology with similar coverage. The average diameter ranged from approximately 2-4 nm. Although the undyed DNA cannot be seen in the TEM images, the EDS peaks of Na, small insets in the bottom of each figure, indicated the presence of DNA. In particular, the EDS results also clearly show the corresponding metal peaks (Au, Pt, and Pd, respectively) and the Cu peaks were from the copper grid (Inset of Figure 7).

It’s worth noting here, DNA, a readily available biopolymer, is an excellent chelating/complexing agent for nanostructures because its rich chemical functionality allows it to interact with a variety of nanomaterials of interest, especially for transition metals. Several review articles[43] have been reported that metal ions binding to the bases, to nucleosides and, to nucleotides of DNA. Sissoëff et al,[44] reported that metal ions can be categorized into three classification according to the biding coordination sites. Those sites are base keto oxygen & ring nitrogen, phosphate oxygen, and sugar hydroxyl. Particularly, negatively charged phosphate oxygen and ring nitrogen, N7 on the bases adenine and guanine while N3 on bases cytosine and thymine, are the favorite biding sites for transition metal ions[43]. N7 biding site for Pt(II) have been confirmed by the Takahara et al.[45] with the experiment for the anticancer drug cisplatin complex. In addition, experiment for interaction between DNA and divalent cations conducted by Duguid et al.[46] with Raman Spectroscopy also confirmed the favorite N7 biding site for Pt(II) and Pd(II) ions. In addition, the Pt NPs size of 2 nm in Dong’s work[35] which is in line with our results of 2.5 nm, is another evidence that DNA already wrapped onto SWNTs.
Figure 4.6 SEM image of the DNA/SWNTs hybrid structure network. The DNA formed as bundle instead of wrapping around individual SWNT.
Figure 4.7 TEM images of (a) Au/DNA/SWNTs hybrid nanostructures, (b) Pt/DNA/SWNTs hybrid nanostructures, (c) Pd/DNA/SWNTs hybrid nanostructures, respectively, and (d) is the average particle size (2~5 nm).

4.3.4 Sensing Performance of Metal/DNA/SWNTs Hybrid Nanostructures

Figure 8 shows the sensing responses of the unfunctionalized SWNTs, DNA/SWNTs and Metal/DNA/SWNTs (Au, Pt, Pd) hybrid nanostructures towards H₂, H₂S, NH₃, and NO₂ at room temperature were investigated with customized sensing system described previously[13, 17]. These sensors were challenged with different concentration of analytes
with 15 minutes exposure and 20 minutes recovery times. The sensor response was
determined by the resistance change before and after exposure to analyte and defined as
\((R_f - R_o)/R_o\) and is shown in Figure 8 as a function of analyte concentration; \(R_f\) is the final
resistance at the peak height and \(R_o\) is initial baseline resistance prior to analyte exposure.
The response time is defined as the time for the sensor to reach 90% of its steady-state
value, and the recovery time is identified as the time required for the sensor after the
exposure to return to 50% of its maximum response. In nearly all cases, metal/DNA/SWNTs hybrid nanostructures improved response times (for example, Pd/DNA/SWNTs hybrid nanostructures with response times of 11 minutes for 20 ppm\(\_\)H\(_2\)S) with respect to the bare SWNTs networks (for example, with response times of 14
minutes for 20 ppm\(\_\)H\(_2\)S). Moreover, the sensor response of metal/DNA/SWNTs were
further enhanced (for example, the normalized sensing response of Pd/DNA/SWNTs
hybrid nanostructure of 1.65 can be seen in the Figure 8 (b2) of the calibration curve toward
H\(_2\)S) with respect to the bare SWNTs networks which is about 0.4 as expose to H\(_2\)S. The
detail information is listed in Tables 1 for all sensing result.

Particularly, in the case of H\(_2\) and H\(_2\)S, Pd/DNA/SWNTs hybrid nanostructures show
the supreme sensing performance for all metrics with dramatically higher sensitivity and
faster response/recovery times, clearly superior to the other devices, Figure 8(a1). Upon
exposure to 100 ppm\(\_\)H\(_2\) (lowest concentration), a 25% change in electrical resistance was
achieved with the response and recovery times of 13 minutes and 6.1 minutes, respectively.
Upon exposure to 2000 ppm\(\_\)H\(_2\) (highest concentration), a 787% change in electrical
resistance was achieved with the response and recovery times of 10 minutes and 1.6
minutes, respectively. The sensing mechanism of the Pd/DNA/SWNTs hybrid nanostructures toward H₂ can be explained by the alteration of the transport properties owing to the interaction of adsorbed species to the Pd and SWNTs surfaces. The possible mechanism involves the adsorption of the H₂ onto Pd surface, where the adsorbed atomic hydrogen reacted with the O₂ in the air and formed hydroxyl group. The hydroxyl group on Pd surface will further react with the adsorbed hydrogen to form water[13]. Therefore, the overall reaction will be the oxidation of H₂ to form H₂O and release electrons into SWNTs network. This caused the recombination of the electrons and holes in the SWNTs network, and then increased its resistance. Furthermore, Pd NPs on SWNTs severed as a nanogate electrode, which scattering the carriers conduct in the SWNTs. The magnitude of the resistance change increases along with the number of Pd NPs[13]. As for the sensing mechanism of the Au/DNA/SWNTs hybrid nanostructures, our previous results of electrochemical deposited Au/SWNTs[17] has indicated that chemisorbed H₂S decompose to form Au-SH or Au-S species on the Au NPs and then the surface work function, resulting the electron flow to SWNTs. This electron donating behavior caused the resistance of Au/SWNTs increase when exposure to H₂S gas. In the case of Pd, oxidation of H₂S into SO₂ occurred on the Pd NPs surface. H₂S react with the surface adsorbed oxygen species to form SO₂[47] and release the electron into DNA/SWNTs causing the increase of the resistance upon exposure of the H₂S.
Figure 4.8 (a) Real-time sensing performance and (b) calibration curve of ink jet printed SWNTs (orange), DNA/SWNTs hybrid nanostructures (red), Au/DNA/SWNTs hybrid nanostructures (blue), Pt/DNA/SWNTs hybrid nanostructures (green), and Pd/DNA/SWNTs hybrid nanostructures (magenta) towards (1) N$_2$, (2) H$_2$S (3) NH$_3$ (4) NO$_2$. 
Table 4.1 Comparison of sensing performance of various Metal/DNA/SWNTs sensor toward H2, H2S, NH3, and NO2.

<table>
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<tr>
<th>Structures</th>
<th>Sensitivity (% ppm⁻¹)</th>
<th>Resp. time (min)</th>
<th>t90</th>
<th>Rec. time (min)</th>
<th>t50</th>
<th>Sensitivity (% ppm⁻¹)</th>
<th>Resp. time (min)</th>
<th>t90</th>
<th>Rec. time (min)</th>
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<td>1.35</td>
<td>9.6</td>
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*The response and recovery time for H₂, H₂S, NH₃, and NO₂ were determined at 1000, 20, 50, and 5 ppm, respectively, which are the personal exposure level for individual analytes except H₂.

Control sensing experiments towards H₂ for metal ions/DNA/SWNTs (Pt⁴⁺, Pd²⁺) hybrid nanostructures before and after reduction were conducted to prove that the sensing performance only came from the metal NPs (Pt and Pd) but not from its metal ions. In Figure 9, as expected, the metal ions/DNA/SWNTs demonstrate no response towards H₂ before reduction confirming that the sensing response coming from the reaction of the analyte and metal NPs.
Figure 4.9 H₂ sensing responses (a) before and (b) after electrochemical reduction.

The sensitivities for each sensor to each analyte toward H₂, H₂S, NH₃, and NO₂ were calculated by taking the slope from the linear part of the sensing calibration curve and compiled in Figure 10. For H₂ sensing, only two positive responses from Pt/DNA/SWNTs and Pd/DNA/SWNTs hybrid nanostructures are achieved, while the other three nanosensors barely responded. For H₂S sensing, all of the five nanosensors gave positive responses with a significant high response from Pd/DNA/SWNTs hybrid nanostructures. For NH₃ sensing, all of the five nanosensors exhibited positive responses as well but without any prominent response. For NO₂ sensing, all of the five nanosensors show negative responses and the responses were relatively high. Thus, the combined responses give a unique pattern or signature for each analyte by which the system can identify and quantify an individual gas.
Figure 4.10 Sensitivity of Ink jet printed SWNTs networks (orange), DNA/SWNTs (red), and Au/DNA/SWNTs hybrid nanostructures (blue), Pt/DNA/SWNTs hybrid nanostructures (green), and Pd/DNA/SWNTs hybrid nanostructures (magenta) towards NO$_2$, NH$_3$, H$_2$S, and H$_2$. 
4.4 Conclusions

Metal/DNA/SWNTs hybrid nanostructures based nanosensors were synthesized by means of ink jet printing of DNA/SWNTs followed by electroless deposition. Shape, morphology and size of the metal nanoparticle particles were controlled by adjusting the electroless deposition conditions and precursor solution composition. Soluble pristine SWNTs inks were obtained by wrapping SWNTs with DNA. With the contribution of the aromatic bases of DNA backbone forming non-covalent $\pi-\pi$ interaction bonding between the interface of DNA and SWNTs, negatively charged DNA/SWNTs can be effectively dispersed in the aqueous solution due to electrostatic repulsion. Furthermore, the backbone of DNA also provides several binding sites for metal ions. Au, Pt, and Pd/DNA/SWNTs hybrid nanostructures were obtained by reducing the already bonded metal ions on DNA.

The sensitivity and selectivity of the gas sensors was determined by analyzing their response to various gases such as H$_2$, H$_2$S, NH$_3$, and NO$_2$ at room temperature. Sensing results indicated the enhancement of the sensitivity and selectivity toward certain analytes by functionalized with different metal nanoparticles. The combined responses give a unique pattern or signature for each analyte by which the system can identify and quantify an individual gas.
4.5 References


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5 Porphyrin and Phthalocyanine Based High Density Chemiresistive Sensor Arrays for Air Quality Index Monitoring

Abstract:

Varies Metallophthalocyanines (TS-CuPc and NiPc) and metalloporphyrins (FeTPP, FeOEP, NiTPP, and RuTPP) were selected to fabricate sensor arrays for Air Quality Index (AQI) monitoring. Ink-jet printing was utilized to prepare smooth film on the prefabricated electrodes and the printing process was optimized with the ink volume and correlate with its electrical properties. The sensitivity and selectivity of the gas sensors towards various gases such as NO₂, SO₂, O₃, and CO was determined at room temperature. The light dependent study was also carried out to understand the sensing performance under the illumination of LED light. The combined responses of the sensor arrays provide a unique pattern or signature for each analyte, and thus the system can identify and quantify an individual gas for the AQI monitoring.
5.1 Introduction

Owing to the serious air pollutions in the urban area and related health issues, the development of an adequate tool to understand pollution levels in an area is of extreme importance. In order to confront air pollution problems and to plan the strategies to diminish the air pollution, both the scientific community and the relevant authorities have focused on monitoring and analyzing the atmospheric pollutants concentration. Under the numerous efforts of related authorities, Pollution Standards Index (PSI) was established in 1976\(^1\). Afterwards, in order to provide accurate, up to date and comprehensible advices concerning the daily levels of atmospheric pollution in terms of health protection, Air Quality Index (AQI) based on five pollutants, namely O\(_3\), NO\(_2\), CO, SO\(_2\) and PM\(_{10}\), was adapted in 2006\(^1\). Although Gas Chromatography (GC), Mass Spectrometry (MS), Fourier Transform Infrared Spectroscopy (FTIR) and a lot of other analytical instruments can detect the airborne pollutants, these instruments are expensive, large and difficult to provide real time monitoring. Consequently, facile approaches, which provide considerable benefits in terms of low cost and manufacturability for mass production, to synthesize rapid response, reversible and selective gaseous chemical detection sensor array at room temperature, are essential for environmental monitoring.

Due to their unique electrical and structural properties, single-walled carbon nanotubes (SWNTs) have gained attention in the field of gas sensing applications\(^2,3\). The charge transfer of the SWNTs is very sensitive due to the rich \(\pi\) electron conjugation outside the SWNTs\(^2\). This unique property makes SWNTs electrochemically active and sensitive to the charge transfer from various gas molecules such as NO\(_2\) and NH\(_3\)\(^2\).
Furthermore, the compact size of the SWNTs (nanometer in radius) makes them a suitable construction block for high density sensor array. However, the lack of sensor performance in terms of sensitivity and selectivity is intrinsic in carbon chemistry and limits the use of SWNTs as an individual sensor. To overcome these limitations, researches have put a lot of efforts on surface modification of SWNTs with different materials to alter their chemical nature and enhance the sensing performance towards specific analyte.

Porphyrin (Por) is an organic macrocyclic compound consisting of four pyrrole linked together by four methane bridges. The resultant compound has unique structural and optical properties, and are chemical stable. They are able to bind nonspecifically with different analytes through van der Waal forces, hydrogen bonding, electrostatics and coordination interactions with the central metal ion. For decades, porphyrins and metalloporphyrins have been the topics of numerous studies. This is because of the fact that certain porphyrin derivatives, such as meso-tetraphenylporphyrin (TPP) and octaethylporphyrin (OEP), play a key role in different essential biological processes such as photosynthesis, dioxygen transport and storage, and electron transfer. The physical properties change of porphyrin when analyte bind on it makes porphyrins an attractive sensing material. The sensing capabilities of porphyrin thin film have been demonstrated based on optical, mass detection, and thin-film-based field effect transistor (FET).

Phthalocyanines (Pc) are analogues of porphyrins. Phthalocyanines have been widely used in the area of dyes and pigments, active components in dye-sensitized solar cells, medical imaging and photodynamic therapy, and especially as gas sensors. In particular, Metal Phthalocyanine (MPc) gain numerous attention as a component in gas
sensors applications especially for NO$_2$, SO$_2$, and O$_3$\textsuperscript{13}. The selectivity and sensitivity of phthalocyanine can be tuned by changing the central metal ion and the substituent groups around the periphery of the molecule\textsuperscript{13}. Thin films and crystals are conveniently prepared by the Langmuir-Blodgett (LB) technique, spin coating or by thermal evaporation\textsuperscript{13}. When the resultant film or single crystal\textsuperscript{14} is exposed to an oxidizing or reducing gas, its conductivity changes accordingly. For example, when the electron withdrawing NO$_2$ chemisorb onto MPc, surface charge-transfer interactions occur, which means electrons flow from MPc to NO$_2$ and more holes are formed in MPc. Since the main charge carriers for the p-type semiconducting phthalocyanines are holes, the charge transfer then increases the conductivity\textsuperscript{16}. The change of the conductivity forms the basis of a simple sensor. However, the currents measured from the device are very low (e.g. nanoamperes) leading to small signal-to-noise ratios and increasing the difficulty of measurement.

A chemiresistive sensor based on conductivity change is the simplest possible transduction mechanism to fabricate a gas sensor, which requires simple technology for electronic application. However, the very low electrical conductivity of the porphyrin and phthalocyanine structures makes it difficult to develop porphyrin and phthalocyanine thin film or crystals based chemiresistive sensors. The hybrid structures of Por/SWNTs or Pc/SWNTs are proposed to provide an alternative way to overcome the above mentioned difficulties. First of all, the introducing of SWNTs in Por/SWNTs or Pc/SWNTs hybrid nanostructures could improves the conductance than the corresponding Por or Pc device. Second, the binding ability of Por and Pc towards different analytes improves the sensing performance of the hybrid device than the SWNTs device.
Por and Pc has a flat and planar structure in nature that facilitates π-π interaction and binds to the SWNTs surface almost without altering SWNTs electronic properties. Furthermore, Por (Pc) can be tailored at the synthetic level by adding different functional groups at the outer ring and/or by introducing different metal atoms at the core of the ring, which could provide different transduction mechanisms depending upon the type of interaction between the Por (Pc) and the analyte. The richness of derivatives of Por and Pc library facilitates the independent development of Por/SWNTs or Pc/SWNTs hybrid nanostructures based high density sensor arrays.

In this work, we utilize the ink jet printing process to prepare the Por/SWNTs and Pc/SWNTs hybrid nanostructures to fabricate the high density individual address sensor array for AQI monitoring application. The sensing performance toward NO₂, SO₂, CO and O₃ under ambient condition and light illumination were correlated with ink jet printing process made by varies MPc and MPor.

5.2 Experimental Procedure

5.2.1 Electrode Microfabrication

Individually addressable sensor arrays consisting of 14 microelectrodes with 3 micron gaps integrated with counter and reference electrodes and temperature sensor [Figure 1(a)] were microfabricated onto a substrate using our previously developed photolithography. The substrate was a highly doped p-type Si wafer (Ultrasil Corporation, Hayward, CA) with a 300 nm oxidation layer deposited by low pressure chemical vapor deposition. A positive photoresist AZ 5214-E (AZ Electronics Materials
USA Corporation, Somerville, NJ) was spin-coated on the substrate at 1000 RPM for 2 s followed by 3000 RPM for 30 s then dried on a hot plate at 110°C for 5 minutes. The patterns were photolithographically defined by UV light at a 70 mJ/cm² exposure dose then immersed in a developer for 45 seconds (AZ 400K : DI water = 1 : 4, AZ Electronics Materials USA Corporation, Somerville, NJ). Platinum film electrodes with a Ti adhesion under layer were e-beam deposited at 180 nm and 20 nm, respectively. The substrate was then soaked in acetone overnight for the lift-off process. Prior to experiments, these prefabricated microelectrodes were diced, cleaned with acetone and water, and blown dry with ultra-high purity N₂ gas.
5.2.2 Ink jet printing for AQI sensor array fabrication

Various metallophthalocyanine and metalloporphyrin were used to fabricate the AQI sensor array. 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin iron(III) chloride
[Fe(III)TPP], 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine iron(III) chloride
[Fe(III)OEP], 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine ruthenium(II) carbonyl
[Ru(II)TPP], and 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine nickel(II) [Ni(II)TPP],
Copper(II) 1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine (CuPc), Copper(II)
phthalocyanine-tetrasulfonic acid tetrasodium salt (TS-CuPc), and Nickel(II)
1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine (NiPc) were used as received
(Sigma-Aldrich). 1 mM of MPc (MPor) stock solution was prepared in CHCl₃.
Carboxylated-SWNTs (SWNT-COOH 80-90% purity, Carbon Solution, Inc., Riverside,
CA, USA) and PEO (M.W. = 35 K, Sigma-Aldrich) was added to the Pc (Por) stock
solution to make the ink for AQI sensor arrays (final concentration of each component in
the ink: 0.1 mM MPc or MPor, 0.1 wt% PEO, and 0.026 mg/mL SWNTs).

Prior to ink jet printing process, the prefabricated microelectrodes were cleaned
with oxygen plasma at 200 Watts for 2 min (Oxford Plasmalab 100/180) under the pressure
of 20 mTorr and then placed on the plate of Fujifilm Dimatix DMP 2831 piezoelectric ink
jet printer. The printer cartridge was filled with the prepared ink and 0.06 µL of such ink
was used for printing of each film. Different jetting voltage and frequency conditions were
tested. Uniform and smooth films were optimized (data not shown here) to be printed at
the applied voltage of 20 V and frequency of 10 kHz. The printing cycle was set up for 20
times to reach the required resistance range, and the clean cycle was fixed after every 5
prints to avoid clog and miss alignment.
5.2.3 Measurements and Material Characterization

The morphologies of the ink jet printed films were investigated by using Hirox Digital Microscope (KH-7700). The electrical resistance and electron transfer characteristics properties of these hybrid nanostructures were determined by two-probe measurements with a Keithley 236 source.

5.2.4 Gas Sensing in the Absence of Light at Room Temperature

Furthermore, the sensing performance of ink jet printed films as AQI sensor arrays were studied by installing the sensing chips in a customized sensing cell [Figure 1(b)] (maximum three chips in three separate cells at one time) with inlet and outlet ports for gas flow and clipping them to a Keithley 236 source to obtain an electrical connection. The resistance was continuously recorded under an applied voltage fixed at 0.5 V. During the sensing measurement, the total gas flow rate was fixed at 200 sccm with desired analytes (NO$_2$, SO$_2$, and CO) diluted with dry air. For the O$_3$ sensing, the O$_3$ gas was generated by flowing dry air (0.5 L/min.) through a pen-ray UV lamp to a quartz chamber and was then connect to the customized sensing cell. The intensity of the UV illumination is continuously adjustable by means of shifting the metal shutter around the lamp. The flow-through oxygen molecules in air can be oxidized to ozone molecules in the range of 0 to 0.8 ppm, according to the UV-radiation intensity. The calibration of ozone concentration and dry air flowing rate was achieved with an ozone sensor (Model A-21ZX, ECO Sensors, Inc.).

In all sensing experiments, sensors were first stabilized in dry air for 60 minutes, and then challenged with different concentrations of analytes with 15 minutes exposure
and 20 minutes recovery times. The sensor response was determined by the resistance change before and after exposure to analyte and defined as \((R_f-R_o)/R_o\), where \(R_f\) is the final resistance of the peak height, and \(R_o\) is the initial baseline resistance prior to analyte exposure. The response time is defined as the time for the sensor to reach 90\% of its steady-state value, and the recovery time is identified as the time required for the sensor after the exposure to return to 50\% of its maximum response.

5.2.5 Light Dependent Gas Sensing Performance in the Presence of LED Light

In order to investigate the light dependent properties of the AQI sensor arrays, the red (\(\lambda= 630\, \text{nm}, \, 7.2\, \text{mW}, \, \text{photon flux } F = 1.44\times10^{14} /\text{cm}^2\text{s}, \, \text{LED630E}\)), green (\(\lambda=525\, \text{nm}. \, 2.6\, \text{mW}, \, \text{photon flux } F = 4.34\times10^{13} /\text{cm}^2\text{s}, \, \text{LED525E}\)), and UV (\(\lambda=370\, \text{nm}, \, 2.5\, \text{mW}, \, \text{photon flux } F = 2.98\times10^{13} /\text{cm}^2\text{s}, \, \text{LED370E}\)) LED lights (Thorlabs, NJ, USA) were integrated into the customized sensing cell. The photocurrent was carried out at room temperature with the Keithley 236 source meter continuously recording under an applied voltage fixed at 0.5 V. For each LED light photocurrent measurement, the light was on for 15 minutes exposure and off for 20 minutes recovery times for three cycles under the flow of dry air at 200 sccm. Furthermore, each LED light was on continuously through the entire sensing process.
5.3 Results and Discussion

5.3.1 Optimization of Ink-jet Printing Process and Sensing Performance

Metalloporphyrins and metallophthalocyanines have been developed as colorimetric sensors due to their abundant color change induced by being exposed to toxic gases\(^7\). Our preliminary data clearly showed the color change of the 0.1 mM Copper phthalocyanines (CuPc) after being exposed to 2 ppm SO\(_2\) [personal exposure level (PEL) = 2 ppm)] for 10 minutes, Figure 2. The UV-Vis spectrum of the as prepared solution (black open square) contains two principal visible region features, Q band (around 300 nm) and Soret band (around 700 nm)\(^{18,19}\). The Q band represents the adsorption of \(\pi\) electrons from the highest occupied energy level (HOMO) to the lowest occupied level (LUMO), and the Soret band is produced from the resonating of \(\pi\) electrons when exposed to the light\(^{19}\). After exposure to SO\(_2\), the intensity of both peaks deceased (red open circle). This indicates the interaction between SO\(_2\) and CuPc resulted in the color change.
Figure 5.2 UV-Vis spectra of 0.1 mM CuPc (in CHCl₃) before (black open square) and after (red open circle) the exposure of SO₂ (PEL = 2 ppm, time = 10 minutes).

Here in this work, ink jet printing was utilized to fabricate high density sensor arrays for AQI monitoring application. In order to obtain a uniform and smooth film, the prefabricated microelectrodes were cleaned with oxygen plasma prior to ink jet printing process. For details regarding the electrodes surface treatment, reference our previous report¹⁷. After the oxygen plasma treatment, the amine-terminated silane²⁰ was used to further increase the surface hydrophilicity for continuous smooth film. Figure 3 shows the contact angle decreased from 30° (after oxygen plasma treatment) to 17° (after silane functionalization for 30 minutes).

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Figure 5.3 (a) SiO₂ chip after 2 minutes O₂ plasma (200 W) treatment showed a contact angle of 30°; (b) the same chip after 30 minutes silane treatment showed a contact angle of 17°.

As mentioned in the introduction, the poor conductivity of Por and Pc are improved by mixing with SWNTs. PEO is added for better film quality by increasing the viscosity\(^{21}\). Figure 4 shows the optical images of the microelectrodes after ink jet printing, from where we can tell that both TS-CuPc [Figure 4(a)] and NiPc[Figure 4(b)] films are uniformly and smoothly deposited.

Here, we varied the ink volume (0.015, 0.03, 0.06 and 0.1 µL, respectively) to optimize the TS-CuPc films toward SO₂ sensing in the absence of light. As shown in Figure 5(a), the maximum sensing response of TS-CuPc films toward SO₂ happened when the film was printed with 0.06 µL TS-CuPc solution. Figure 5(b) showed the relation of the ink volume, the film resistance, and their sensing response. Although the resistance decreases [solid square in Figure 5(b)] as the ink volume increases, the sensing response [open square in Figure 5(b)] increases first and then decreases. Since PEO was added in the ink as an additive, the effect of PEO for sensing performance was investigated. Figure
6 shows the sensing performances of the SWNTs film and the PEO/SWNTs film (0.1 wt% of PEO mixed with 0.026 mg/mL SWNTs). In Figure 6(a), both printed films were tested against NO\textsubscript{2} and showed similar results, indicating PEO did not change SWNTs sensing towards NO\textsubscript{2}. The NO\textsubscript{2} sensing results are also in line with our previously results in the absence of the light\textsuperscript{17}. The SWNTs film and the PEO/SWNTs film are also challenged with SO\textsubscript{2}, CO and O\textsubscript{3}, and neither of them showed response. Figure 6(a2) is the SO\textsubscript{2} sensing results. (The sensing results of the CO and O\textsubscript{3} are not shown here). Therefore, PEO is proven not to affect the sensing results and the sensing response only comes from the Pc/SWNTs or Por/SWNTs hybrid nanostructures.
Figure 5.4 Optical images of the electrode after ink jet printing of (a) TS-CuPc and (b) NiPc, respectively. 0.1 mM of individual phthalocyanine solution (TS-CuPc or NiPc) were blended with 0.1 wt% of PEO and 0.026 mg/ml SWNTs, respectively. The substrate temperature was kept at 40 °C during ink jet printing process. The printed ink volume was 0.06 µL.
Figure 5.5 The sensing performance towards SO\textsubscript{2} were correlated with ink jet printing process: (a) SO\textsubscript{2} real-time sensing performance of films printed with 0.015, 0.03, 0.06, and 0.1 µL TS-CuPc solutions (0.1 mM), and (b) the relation of sensing response (ΔR/R\textsubscript{0}) and the corresponding printed films resistance.
Figure 5.6 Real-time sensing performances and calibration curves of SWNTs film (blue) and PEO/SWNTs film (orange) towards (a) NO₂ and (b) SO₂, respectively.

5.3.2 Printed Sensor array for Real Time AQI Monitoring

Two metallophthalocyanine films (TS-CuPc and NiPc) and four metalloporphyrins films (FeTPP, FeOEP, NiTPP, and RuTPP) were selected for AQI monitoring application. The I-V curve in Figure 7(a) reveals the ohmic contact for all the films. The electron transfer characteristics [Current (Iₜₜₕ) vs. back gated voltage (Vₜₜₕ)] curve shown in Figure 7(b) indicates their p-type semiconducting heavier, consistent with reported literatures⁵,¹⁰,²².
The printed films were tested towards NO₂, SO₂, CO and O₃ as an AQI monitoring sensor array. In Figure 8, the sensor array was exposed to NO₂ [Figure 8(a)], SO₂ [Figure 8(b)], CO (data not shown) and O₃ [Figure 8(c)] sequentially.

![Figure 5.7](image)

**Figure 5.7** (a) I-V curves of the TS-CuPC, NiPc, FeOEP, FeTPP, NiTPP, and RuTPP ink jet printed films, respectively, and (b) their electron transfer characteristics [Current (IₓSD) vs. back gated voltage (VₓG)].

5.3.2.1 NO₂ Sensing and the Sensing Mechanism

Figure 8(a) demonstrates sensing performance of the ink jet printed films towards NO₂. The resistance of the MPc (TS-CuPc and NiPc) decreased when exposed to NO₂, in line with published literature of a NO₂ doped CuPc. The possible sensing mechanism of NO₂ on the MPc surface was proposed as the following equation:

\[
S + NO_2(g) \xrightarrow{\text{Adsorption}} S, NO_2\text{ads} \leftrightarrow S^+, NO_2^-
\]  

(1)

The S in the equation represents the adsorption sites. From the equation, when NO₂ is adsorbed onto the surface of the MPc, the electrons are trapped by NO₂ gas molecules and
holes are left in MPc. This leads to the increase in the carrier concentration in MPc; therefore, the conductivity is enhanced\textsuperscript{10}.

The MPor (FeOEP, FeTPP, NiTPP and RuTPP) has the similar sensing mechanism to MPc. The kinetic study of the Por thin film also indicated that electron transfer from the MPor to NO\textsubscript{2}\textsuperscript{25} (leaving the holes in valence band), increasing the electrical conductivity.

### 5.3.2.2 SO\textsubscript{2} Sensing and the Sensing Mechanism

Figure 8(b) shows the sensing performance of the ink jet printed films towards SO\textsubscript{2}. From the sensing result, the resistance of both MPc and MPor increases when exposed to SO\textsubscript{2}. This is possibly due to the chemisorption of the SO\textsubscript{2}\textsuperscript{26,27}, which forms the sulfate (SO\textsubscript{4}\textsuperscript{2\textendash}) group\textsuperscript{27} on the MPc and/or MPor surface. The sulfate group donates electrons into the the MPc/SWNTs (MPor/SWNTs) and results in the recombination of the electrons and holes in the hybrid nanostructures, which decreases their electron carriers.

As expected, only two porphyrins FeOEP and FeTPP showed sensing response towards SO\textsubscript{2}. This is attributed to the strong axial coordination of the Fe atom (in porphyrins) to the S atom (in SO\textsubscript{2}), similar to the Fe-S bond formed between heme proteins and sulfur-containing compounds\textsuperscript{28}.

### 5.3.2.3 O\textsubscript{3} Sensing and the Sensing Mechanism

Figure 8(c) is the sensing performance of the ink jet printed films towards O\textsubscript{3}. Ozone is known as a strong oxidizing agent that withdraws electrons from the sensing materials. However, due to the highly instability of O\textsubscript{3}, the adsorbed O\textsubscript{3} generates highly active atomic oxygen intermediate species (Eq. 2), and thus the intermediate species has to
be taken into account. The generated atomic oxygen would react with a second O$_3$ molecule to form an additional peroxide specie and gaseous molecule (Eq. 2-4).

\[
S + O_{3(g)} \rightarrow S, O_{2,ads} + O_{2,ads}^* \quad (2)
\]

\[
O_{3(g)} + O_{ads}^* \rightarrow O_{2(g)} + O_{2,ads}^* \quad (3)
\]

\[
MPc + O_{2,ads}^* \leftrightarrow MPc^* + O_2^- \quad (4)
\]

The S in the equation represents the adsorption sites, and O$_{ads}^*$ and O$_{2,ads}^*$ represent the intermediate reactive atomic oxygen and peroxide specie, respectively. Therefore, the resistance of the MPc (TS-CuPc and NiPc) decreases upon exposure to the O$_3$ and the reversibility of the MPc oxidation could occur with desorption of the dioxygen molecules (O$_2$)$^{15}$.

None of the MPor showed response towards O$_3$, due to the lack of four N atoms in the center ring of MPor. Previous study has shown that O$_3$ has a tendency to attack the methyne bond (C=N, the signature finger print for Pc) in MPc, which changed the Q band absorption$^{29}$. This is the reason that MPc has sensing response towards O$_3$ while MPor do not.
Figure 5.8 Real-time sensing performances and calibration curves of ink jet printed films towards (a) NO$_2$, (b) SO$_2$, and (c) O$_3$ in the absence of light, respectively.
5.3.3 Printed Sensor Array for AQI Monitoring under the Illumination of LED Lights

5.3.3.1 NO\textsubscript{2} Sensing under the Illumination of LED Lights

Figure 9 displays the real-time sensing performance of the ink jet printed films towards NO\textsubscript{2} under the illumination of red [Figure 9(a)], green [Figure 9(b)], and UV lights [Figure 9(c)], and only the UV illumination enhanced the sensing performance. This might be due to the excitation of the \(\pi\) electrons in the Q band by UV light. Based on Eq. 1, the delocalized \(\pi\) electrons transfer from the HOMO to LUMO because more NO\textsubscript{2} are trapped onto the surface under UV illumination. This increases in the conductivity and thus enhances the sensing response. In addition, UV light also provides sufficient energy to increase the desorption efficiency of the NO\textsubscript{2} and decreases in the recovery time. Take TS-CuPc sensing response towards 5 ppm NO\textsubscript{2} for example, the response (\(t_{90}\)) and recovery time (\(t_{50}\)) decreases from 10 and 9.2 minutes (in the absence of light) to 5 and 7 minutes (under UV light), respectively.
Figure 5.9 Real-time sensing performances and calibration curves of ink jet printed films towards NO₂ (a) under red light illumination, (b) under green light illumination, and (c) under UV light illumination, respectively.
5.3.3.2 SO₂ Sensing under the Illumination of LED Lights

Figure 10 is the real-time sensing performance of the ink jet printed films towards SO₂ under the illumination of red [Figure 10(a)], green [Figure 10(b)], and UV lights [Figure 10(c)]. Different from the NO₂ sensing, the SO₂ sensing performance of all the films was suppressed under illumination of light. For example, the \( \Delta R/R_o \) for the TS-CuPc decreased from 40% (in the absence of light) to less than 10% (under UV light).

5.3.3.3 O₃ Sensing under the Illumination of LED Light

Figure 11 reveals the sensing performance of the ink jet printed films towards O₃ under the illumination of red [Figure 11(a)], green [Figure 11(b)], and UV lights [Figure 11(c)], respectively. The sensing performance of MPc towards O₃ was enhanced under UV illumination. For example, the sensing response (\( \Delta R/R_o \)) of TS-CuPc towards 0.1 ppm O₃ increased from 10% (in the absence of light) to 20% (under UV light), and that of NiPc increased from 20% (in the absence of light) to 35% (under UV light). Under the UV illumination, the conjugated \( \pi \) electrons excited from HOMO to attract the O₃ in the environment, resulting the increase of the conductivity. One thing worthy noting is the slower recovery of NiPc and TS-CuPc under UV illumination. This is owing to more methyne (C=N) bonds in the ring of the Pc are broken under the illumination of UV light\(^{29}\). This can cause the PC degradation, but only the very superficial layer of the Pc film. Research has shown that it takes around one year to complete degrade a 100-nm-thick MPc film under continuously exposure to 1 ppm O₃\(^{30}\).
Figure 5.10 Real-time sensing performances and calibration curves of ink jet printed films towards SO$_2$ (a) under red light illumination, (b) under green light illumination, and (c) under UV light illumination, respectively.
Figure 5.11 Real-time sensing performances and calibration curves of ink jet printed films towards O₃ (a) under red light illumination, (b) under green light illumination, and (c) under UV light illumination, respectively.
5.4 AQI sensing pattern

The sensitivity for each sensor towards each analyte (NO₂, SO₂, CO, and O₃) was calculated by taking the slope from the linear part of the sensing calibration curve. The sensitivity of the hybrid nanostructures Por/SWNTs, Pc/SWNTs, as well as SnO₂/SWNTs and Pt/SnO₂/SWNTs that studied in the last chapter were shown in Figure 12 to provide a whole sensing pattern in the ambient condition. For NO₂ sensing, all of the eight nanosensors showed negative responses with similar sensitivity. For SO₂, TS-CuPc, NiPc, FeOEP and FeTPP demonstrated positive sensing response and the other nanosensors showed no response. For CO, neither MPc nor MPor had sensing response, while SnO₂/SWNTs had positive response and Pt/SnO₂/SWNTs had negative response. For O₃, TS-CuPc and NiPc had negative response and the other nanosensors showed no response. Thus, the combined sensing responses give a unique pattern or signature for each analyte by which we can identify and quantify an individual gas.

5.5 Conclusions

In this work, a simple, fast and cost effective ink jet printing process was utilized to fabricate high density sensor arrays for AQI monitoring. Smooth films of Metallophthalocyanines (TS-CuPc and NiPc) and metalloporphyrins (FeTPP, FeOEP, NiTPP, and RuTPP) were successfully printed onto the integrated microelectrodes. The sensitivity and selectivity of the gas sensors was determined by analyzing their response to various gases such as NO₂, SO₂, CO, and O₃ at room temperature. The effect of the red, green, and UV light illumination on sensor sensing performance was also investigated. The
combined responses give a unique pattern or signature for each analyte, and thus the system can identify and quantify an individual gas for the AQI monitoring.

**Figure 5.12** Sensitivity of Ink-jet printed film of Ts-CuPc/SWNTs hybrid nanostructures (red), and NiPc/SWNTs hybrid nanostructures (green), FeOEP/SWNTs hybrid nanostructures (blue), and FeTPP/SWNTs hybrid nanostructures (magenta), and NiTPP/SWNTs hybrid nanostructures (magenta), and NiTPP/SWNTs hybrid nanostructures (orange), and RuTPP/SWNTs hybrid nanostructures (pink) as well as SnO$_2$/SWNTs hybrid nanostructures (grey), and Pt/SnO$_2$/SWNTs hybrid nanostructures (dark yellow) towards NO$_2$, SO$_2$, CO, and O$_3$. 
5.6 References

(2) Ting, Z.; Syed, M.; Nosang, V. M.; Marc, A. D. *Nanotechnology* 2008, 19, 332001.
(20) Melburne C. LeMieux; Mark Roberts; Soumendra Barman; Yong Wan Jin; Jong Min Kim; Bao, Z. *Science* 2008, 321.
6 CONCLUSION AND FUTURE DIRECTIONS

Recent researches have been focused on the progress of a simple and robust sensor that can be operated based on the measurable signal created from the interaction of sensing element with analytes. The output signals are usually in the forms of the change in resistance, capacitance, temperature and/or luminescence. In particular, conductometric sensors are amenable compact and portable platforms for operation in the field.

To overcome current performances in sensitivity, selectivity, power consumption as well as the response/recovery time, one dimensional nanostructures, such as single-walled carbon nanotubes (SWNTs), are utilized as both transuding and sensing element. SWNTs with its extraordinary physical, chemical and electrical properties have been intensively studied.

The dissertation is based on the applications of SWNTs and the functionalized SWNTs for real-time gas sensing study as well as their applications of detection and quantification of the Air Quality Index (AQI). First of all, the high density sensor arrays with individual addressable sensor for the detection of multi-target analytes were fabricated by micromachining processes consisting of deposition, etching, etc, and patterning is typically done by using photolithography. One simple, controllable and scalable approach has been developed to functionalize SWNTs with various materials (organic/inorganic). The sensing performances of these hetero-nanostructures towards different analytes both in ambience condition and under the illumination of LED lights have been systematically
studied. The sensing performance was correlated with the electrical properties, particle size and density, crystallinity, and the morphology of the sensing element to find out the optimum condition for specific target analyte.

6.1 Summary

Chapter 1 provides a general introduction to the gas sensors, especially the importance of gas sensors based on one-dimensional (1-D) nanostructures, followed by a comprehensive literature review on the 1-D nanostructures currently being investigated for gas sensing applications. The review in the introduction mainly consists of SWNTs, metal oxides, and the porphyrins and phthalocyanines based gas sensors.

Chapter 2 discussed about the development of the SnO$_2$ decorated SWNTs gas sensors for environmental monitoring. Synthesis and material characterizations of SnO$_2$/SWNTs hybrid nanostructures were performed by electrochemical routes with precise control of deposition potential and charge density to tailor the composition and electrical properties. The optimum electrodeposition condition for NH$_3$, CO, and NO$_2$ was defined from analyzing each sensing performance in ambient condition. Their sensing performances were then enhanced with the assistance of the UV illumination. In particular, the limit of detection towards CO was lowered to 0.5 ppm.

Chapter 3 continued with the sequential functionalization of SnO$_2$/SWNTs hybrid nanostructures with Pt for CO sensing. The surface morphology, growth mechanism and room temperature sensing performance as well as the effect of light illumination and environmental temperature were investigated. With the help of Pt nanoaprticles, the CO poisoning effect was found to cease. We also noticed that the sensitivity towards CO was
enhanced under the illumination of the red, green, and UV light, respectively. Furthermore, the CO poisoning effect was eliminated and the room temperature limit of detection was lowered to 0.05 ppm for the Pt/SnO$_2$/SWTNs hybrid nanostructures under the illumination of UV light. To the best of our knowledge, this is the lowest CO concentration detected compared to those has been reported.

Chapter 4 described the development of SWNT-based hybrid nanostructures sensor arrays via electrochemical reduction and ink jet printing process to detect airborne toxins. DNA is utilized to work as dispersion agent for soluble SWNTs as well as metal ions chelation/nucleation sites. High density sensor arrays are achieved through ink jet printing positioning process followed by electroless deposition. The sensing performance towards airborne toxins (i.e., H$_2$, H$_2$S, NO$_2$, and NH$_3$) is quantified by tailoring the type of deposited metals and the size of the metal nanoparticles with different metal ion precursors and various concentrations. Selectivity and sensitivity towards targeted different analytes were characterized and optimized.

Chapter 5 dealt with the porphyrin and phthalocyanine based SWNTs gas sensor arrays. In this work, a simple, fast and cost effective ink jet printing process was utilized to fabricate high density sensor arrays for AQI monitoring. Smooth films of a series of metallophthalocyanines (TS-CuPc and NiPc) and metalloporphyrins (FeTPP, FeOEP, NiTPP, and RuTPP) were successfully printed onto the integrated microelectrodes. The sensitivity and selectivity of the gas sensors was determined by analyzing their response to various gases such as NO$_2$, SO$_2$, CO, and O$_3$ at room temperature. The effects of the red,
green, and UV light illumination on sensor sensing performance were also investigated. The combined sensing responses provided a unique pattern or signature for each analyte, and thus the system can identify and quantify an individual gas for the AQI monitoring.

6.2 Future Works

A major contribution of this thesis was to show the possibility of fabrication of 1-D nanostructures using a simple electrochemical route as well as the synthesis of high density sensor arrays for practical use in the field. It is worth noting that three significant challenges currently exist in terms of the sensing performance of the device here fabricated. First of all, the response and recovery time are still large (in minutes). Although the response and recovery time can be shortened with the assistance of the light illumination, it is limited and not suitable for all analytes. The use of the LED light also increases the difficulties for maintenance as well as the extra power consumption when applied in the field. Second, all the sensing performance were tested under the controlled environment. It remains a challenge for the sensors we fabricated to be used in the field since the humidity and temperature are always changing not mention the complexity of the air in real environment. Therefore, enhance the stability of the sensing materials and the pattern recognition algorithms for individual gas recognition and multi-components analysis are strongly desired in the near future.