Chapter 5

# Experimental Analysis of Modified CNTs-Based Gas Sensor

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Additional information is available at the end of the chapter

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**Abstract**

As a significant equipment in power system, the operation condition of transformers directly determines the safety of power system. Therefore, it has been an indispensable measure to detect and analyze the dissolved gases in transformers, aiming to estimate the early potential faults in oil-insulated transformers. In this chapter, the adsorption processes between modified carbon nanotubes (CNTs) (CNTs-OH, Ni-CNTs) and dissolved gases in transformers oil including $C_2H_2$, $C_2H_4$, $C_2H_6$, $CH_4$, CO, and $H_2$ have been simulated based on the first principle theory. Meanwhile, the density of states (DOS), adsorption energy, charge transfer amount, and adsorption distance of adsorption process between CNTs and dissolved gases were calculated. Moreover, two kinds of sensors, mixed acid-modified CNTs and $NiCl_2$-modified CNTs, are prepared to conduct the dissolved gases response experiment. Then, the gas response mechanisms were investigated. Finally, the results between response experiment and theoretical calculation were compared, reflecting a good coherence with each other. The CNTs gas sensors possess a relatively high sensitivity and fine linearity, and could be employed in dissolved gas analysis equipment in transformer.

**Keywords:** oil-insulated transformer, modified CNTs, dissolved gases, DFT method, gas-sensing experiment

## 1. Introduction

### 1.1. The significance of dissolved gases detection in oil-insulated transformer

The stability of electrical equipment is the key factor for the running safety and economy of electrical power system. Along with the extra-high-voltage grid construction, power transmission capacity becomes larger, coverage area becomes wider, and the national power grids at all levels are closely linked to each other, so the harm of grid accidents would be more serious [1]. Large power transformer, as the key equipment of power system, plays influential role to ensure the safe operation of power system. Real-time detection of insulation state of transformer, accurately predicting the fault and avoiding possible trouble are important measures to ensure the safe operation of the electrical grid [2], to improve equipment utilization and reduce costs of equipment maintenance, which are also key technical issues of constructing the strong and intelligent electrical grid. A lot of study and practice has proved that the main reason for the transformer accident is the deterioration of its insulation performante. With the development of electronic, computer, sensor and information processing technology recently, detection ways for insulation state of large-scale power transformer have been rapidly developing. For example, dissolved gas analysis (DGA) [3], partial discharge (PD) [4], winding coefficient of dielectric loss measurement, winding insulation resistance measurements, winding deformation and winding hot spot temperature monitoring the micro water insulation monitoring, etc. [5], these ways can help people to get the insulation state of transformer from different aspects.

Dissolved gas-in-oil analysis (Oil-DGA) is the most convenient and effective method of judging the early potential fault of oil-immersed power transformers at present [6–8], and the method is the most extensive one in the real application, which has become an indispensable approach to judge the internal fault of oil-filled electrical equipment and oversee the safe operation of equipment [9]. Research shows that, among main obstacle and defects of transformers discovered by experiment examinations, faults found by dissolved gas analysis of test standard always take up the highest percentage, 60.1% in 2004 and 68.5% in 2005 [10]. The international electro technical commission develops standard IEC60567 "Oil-filled electrical equipment—Sampling of gases and analysis of free and dissolved gases—Guidance" and IEC60599 "Mineral oil-impregnated electrical equipment in service—Guide to the interpretation of dissolved and free gases analysis." Gas chromatography is widely applied to quantitative analysis of various gases dissolved in transformer oil content. For the past few years, it has become the new trend to develop the pint-sized gas-detecting device by using the gas-sensing technology, which is aimed at achieving on-line monitoring to dissolved gas in transformer oil and grasping the operational state of equipment at any time [11, 12]. On-line monitoring of dissolved gas analysis could help reduce the unavailability of equipment in the long run-time [13], thus it can improve the economic benefit, optimize cycle and content of maintenance job to decrease maintenance fee and improve control of power system and the reliability of monitoring performance in overload operation [14].

The high-sensitivity gas sensors are used to detect dissolved gas in transformer oil [15], structure of test system is simple and it is easy to implement. In recent years, a breakthrough has been making in the sensor technology [16, 17]. Especially, the development of nanotechnology has been providing the new material and processing method [18], in which the carbon nanotubes (CNTs) gas sensor has become the new research focus [19]. CNTs have abundant pore structure, large specific surface area, and a strong ability of adsorption and desorption for chemical composition of the gas phase, these properties make CNTs, as gas sensor, incomparable in conventional sensors of the detection sensitivity and miniaturization [20]. At present, this technology obtains rapid development in the biological, chemical, machinery, aviation, military, and other aspects.

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As the pressure of global resources and environment is increasing, the society demand for environmental protection, energy conservation, and emissions reduction and sustainable development is increasing day by day. Along with sustainable development of social economy, the rapid growth of electricity demand, carrying out the energy conservation and emissions reduction and construction of "resource saving and environment-friendly society," has become a very urgent task. The Electric Power Research Institute (EPRI) put forward the concept of smart grid in 2000; they think this is development tendency in the future power grid and a way to solve the problem of the grid in twenty-first century. So-called smart grid is the advanced sensor measurement technology, information technology, communication technology, computer technology, automatic control technology, and the original transport and distribution infrastructure highly integrated to form a new type of power grid. The observability based on advanced measurement, sensing technology, and real-time analysis based on comprehensive analysis of decision-making reflects mainly intelligence in grid [21, 22], and it is one of the hot topics in the study of the current smart grid.

In conclusion, new sensors researched are used to detect equipment on real-time and accurately predict failure, do nip in the bud. These are important measures to ensure the safety of the grid in production, improve equipment utilization, and reduce the equipment maintenance cost, also, is the key technology of construction for unified strong smart grid. Based on the study of the existing transformer oil gas detection and analysis method, this chapter studies deeply application of nanometer gas-sensitive sensor technology for transformer oil gas detection and analysis, develops a new CNTs gas sensor and, tests its gas-sensing property, master the basic law, put forward an algorithm of dissolved gas analysis in oil-based dynamic tunnel fuzzy c-means to rich analysis method of transformer fault characteristics. This research topic from the urgent demand in reality not only has important academic value but also has significant economic and social benefits and broad application prospects.

### 1.2. The methods for dissolved gases detection in oil-insulated transformer

At present, most of high-voltage and large-capacity power transformers used oil filled; this transformer used composite structure including insulating oil and insulation paper (plate) and has the very high-electric strength. During long-running process, insulating oil and other insulating materials of transformer under the effect of electricity and heat will gradually age and decompose, resulting in the production of gases such as low molecular hydrocarbons, CO, and $CO_2$ that get dissolved in insulating oil [23, 24]. When the transformer is in normal operation condition, the outside factors such as electricity, heat, and mechanical stress cannot break chemical bond of insulating oil and insulation paper (plate). Insulating materials only produce little gas when they are normal aging. But the discharge and overheating fault occur in the equipment, deterioration process of insulating materials is greatly accelerated to accelerate rate of biogas production of the above gas [25]. The study demonstrated composition and content of these gas has close relation with property of fault, these gases are called as characteristic gases, as shown in **Table 1**.

It has a great significance for indication of the transformer early fault to monitor change of characteristics of the gas composition and content in insulating oil. Electromagnetic interference shows no influence on dissolved gases analysis, and dissolved gases analysis shows high data reliability.

| Fault type | Insulation medium | Main components | Minor components |
|---|---|---|---|
| Overheating | Oil | $CH_4$, $C_2H_4$ | $C_2H_6$, $H_2$ |
| | Transformer oil paper insulation | $CH_4$, $C_2H_4$, CO, $CO_2$ | $C_2H_6$, $H_2$ |
| Arc discharge | Oil | $C_2H_2$, $H_2$ | $C_2H_6$, $CH_4$, $C_2H_4$ |
| | Transformer oil insulation paper | $C_2H_2$, $H_2$, CO, $CO_2$ | $C_2H_6$, $CH_4$, $C_2H_4$ |
| Partial discharge | Transformer oil and insulation paper | $CH_4$, CO, $H_2$ | $C_2H_6$, $CO_2$ |
| Spark discharge | Transformer oil | $C_2H_2$, $H_2$ | / |
| Bubble discharge | Watered oil | $H_2$ | / |

**Table 1.** Characteristic gases of several styles of faults.

The technology develops maturely and accumulates considerable experience from qualitative to quantitative analysis to form relative regulation, such as International Electrotechnical Commission standard IEC60567 and IEC60599. Since the 1970s, transformer fault diagnosis based on characteristic gases dissolved in transformer oil has widely spread all over world and gradually applied in the field.

According to "the guidelines for the dissolved gas in transformer oil analysis, and judgment," detection of gas content first needs gas separation from oil (i.e., the degassing). The gas separated from oil is a mixture of various gas components. The general gas content detection method has sensitive for all kinds of gases or a gas. To detect a single gas, we usually use gas chromatography to separate various gas components [26]. The advantage of gas chromatographic method is quantitative analysis for a variety of gas content dissolved in oil; meanwhile, there are characteristics in it, such as many test links, complex operation, high technical requirements, and long test cycle. Therefore, this method is usually used to regular checking for main equipment (e.g., once half a year), professional workers conduct it in laboratory. However, in two regular interval periods, the internal condition changes of transformer cannot be found in a timely manner. Application of micro gas-sensor technology is developed to miniaturized gas detection device, which can monitor on-line dissolved gas in transformer oil to master the running status of equipment whenever. When an alarm occurs in on-line monitor, we could use method such as chromatographic analysis to secondary diagnosis [27].

The on-line monitor of dissolved gas in transformer oil still based on the categories and quantities of dissolved gas which can be seen as fault characteristic quantities. The difference is that real-time on-line monitoring of oil chromatography and intelligent fault diagnosis can be realized using this technology. This can not only gain the running state of the transformer timely, based on which latent faults can be detected and tracked, but also diagnose fault automatically due to the expert system so as for operating crew, fault can be handled rapidly. Using on-line monitoring device can improve the management level of substation operation and lay a foundation of transition from preventive maintenance system to predictive maintenance system [28].

Choosing different sensors and cooperating to use different ways to take air and use diagnostic devices due to different test object can make up a variety of on-line or portable monitoring device to detect the dissolved gases in transformer oil [29, 30]. The method of detecting the dissolved gases in transformer oil can be divided into the following categories:

**1.** According to the categories of test object

**a.** Measuring the total content of combustible gases

The amount of combustible gases refers to the total quantities of $H_2$, CO, and all kinds of gaseous hydrocarbons. These kind of devices represented by TCG detection device of Japan's Mitsubishi electric power company can only give the amount of combustible gas but cannot measure the content of one component.

**b.** Measuring the content of single component: $H_2$

When overheating or partial discharge occurred in the equipment, hydrogen would appear. Fuel cell sensor such as HYDRAN produced by SYPROTEC Company in Canada can acquire signals. This device is suitable for the preliminary diagnosis for fault on the spot based on its simple structure, but chromatographic analysis must be applied to further determine the fault.

**c.** Measuring the content of composite gas components

With the development of on-line monitoring technology, on-line chromatographic detection devices have been invented for measuring full-component gases. The gas transformer oil on-line gas monitoring equipment of AVO Company in the USA can measure the contents of up to eight kinds of gases. DRMCC transformer on-line monitoring system can monitor the working status of transformer continuously, timely, and systematically. The main monitoring objects include dissolved substances such as hydrogen, water and wind temperature, position of tap, etc. The CONEDISON Company analyzed and measured the contents of $CH_4$, $C_2H_4$, CO, $CO_2$, and $C_2H_6$ using infrared spectroscopy method and measured the content of $H_2$ with an oxide electrochemical sensor. The on-line transformer fault prediction system developed by Chongqing university can measure the concentration of $H_2$, CO, $CH_4$, $C_2H_4$, $C_2H_2$, and $C_2H_6$ timely and can availably predict the concentrations of the dissolved gases in transformer oil and diagnose insulation condition of transformer in future with the method of gray clustering, paste pattern multi-level clustering, and kernel-based possibilistic clustering. Due to the limitation of sensing technology, the current on-line monitoring devices are not satisfactory in reliability and sensitivity, but on-line monitoring is the development direction of analysis technology of dissolved gases in transformer oil.

**2.** According to the categories of methods of extracting gas

**a.** Polymer separation membrane permeability method

Polymer membranes of organic synthesis have different degrees of permeability and can be used in industrial gas separation and purification process. In the mid-1960s, use of polyester hollow fiber membrane to recover hydrogen by Du Pont Company is one of the earliest attempts to use membrane to separate gases. The gases in oil follow Henry's law and go through the membrane into the air chamber so the gas concentration in the chamber and the dissolved gas concentration in the oil are balanced. The transmittance of the film is as high as possible to minimize the detection cycle, so that timely detection, timely alarm can be realized. Kurz first produced the polymer membrane and made its use for separation of transformer oil and gas, then the polyimide, polyhexafluoroethylene, polytetrafluoroethylene, and other polymer membranes were studied. China Electric Power Research Institute, Chongqing University, and other research institutions made repeated tests on the permeability of a variety of membranes, the results showed that Polytetrafluoroethylene (PTFE) film not only had good air permeability but also had good mechanical properties and resistance to oil, high temperature, and many other advantages. Therefore, it is often used as breathable film on the detectors of dissolved gas [31].

**b.** Method of vacuum pumping to extract gas

According to the principle of vacuum degassing, vacuum pump or bellows vacuum is used to extract dissolved gas in oil to achieve on-line monitoring of dissolved gas in transformer oil.

**c.** Other methods of extracting gas

Use different methods of blowing gas to replace oil-soluble gas so that the concentration of one kind of gas on surface and the concentration of that in oil gradually reach equilibrium and then analyze the gas on surface using a detector. Common methods contain carrier gas elution, air circulation, colorimetric pool method, etc.

**3.** According to the sensors that collect the signals

The detector that is used to detect separated or unseparated gases and has responses to a sample or samples is an important component of a detection device. It can be divided into palladium gate Field Effect Transistor (FET), semiconductor sensor, catalytic combustion sensor, combustion cell sensor, and other types of sensors [32].

The results show that combining two or more sensors, using modern computer technology, and developing the corresponding data processing software, we can measure the content of two kinds of fault gases and can achieve significantly better detection performance than one conventional sensor with a single monitoring device [33]. The development of gas-sensor array technology includes two aspects, one is to develop integrated micro gas-sensor array using micro-manufacturing, micro-machining technology; the other is to improve the accuracy of a single gas identification and realize quantitative analysis mixed gas using multi-sensor information fusion technology. Whether in the integration of sensor array, or in the analysis theory and technology of sensor array, it has become the hot spots of current sensor researches.

Using high-sensitivity gas sensor to detect dissolved gases in oil is easy to realize due to its simple gas line. But the existing gas sensor's detection sensitivity and reliability have not yet reached the level of sensitivity and reliability of off-line detection, so there are a lot of work to do. With the continuous development of detection technology, a variety of new sensors continues to come out, such as photoionization detector using energy of photons to ionize each type of gas, methane gas sensor, CO gas sensor based on vibration at room temperature, $CO_2$ gas sensor using solid battery, Pt doped $SnO_2$ separation membrane gas sensor by impregnation, CNTs sensor, etc. These new sensors create a good prospect of developing for the detection of high-sensitivity transformer oil-dissolved gas using on-line monitoring device. However, due to the harsh natural environment of on-line monitoring, complex strong electromagnetic interference, a large number of studies is also needed in selecting these sensors for gas detector [34].

## 2. Introduction of CNTs gas sensor

### 2.1. Introduction of gas-sensor technology and current situation

Sensor is a type of device that can transfer physical or chemical parameters into available electric information. Sensor can be defined as "device or apparatus which can sense the specified measurement and transfer it into available output signals by some laws" [35].

Gas sensors, namely gas-sensitive devices, are a type of device or apparatus that can sense specific gases and their concentrations in the environment. Information about the species and concentrations of gases can be transferred into electric signals for detection, monitoring, analysis, and alarm. Gas sensor is an important branch of sensor technology. Since the research on gas sensors started in the 1930s, it has passed more than half a century and there are several hundred kinds of sensors, which have been utilized in many aspects of human life, including national defense and military, industrial and agricultural production, energy and resource exploit, medicine, environment protection, disaster prediction, transport, etc. [36].

The fundamental characters of gas sensors include: sensitivity, selection, stability and resistant ability to corrosion, etc. Those characters are ensured by the selection of materials. Based on the characteristics of aimed gases, the environment conditions, detection requirements, and proper materials can be chosen or prepared for best gas-sensing properties of gas sensors. According to gas-sensing materials and gas-sensing response, gas sensors can be roughly divided into electric, optical, electrochemical, and other types, shown in **Figure 1**. The advantages and disadvantages of different gas sensors are shown in **Table 2**.

Microelectromechanical technology (MEMT) is the main manufacturing technology of gas sensors. MEMT is a type of new technology based on microelectronic technique and micromachining technology, including bulk micro-machining technology, surface micro-machining technology, and Lithographie, Galvanoformung and Abformung (LIGA) technology based on X-ray. Bulk micro-machining technology mainly aims at single silicon crystal, of which the key technique is corrosion and wire bonding technology with processing thickness of dozens to hundreds micron; surface micro-machining technology is based on semiconductor technique like oxidation, spread, photoetching, thin-film deposition, and other techniques, with thickness of several micron; LIGA technology adopts conventional X-ray for procession, with thickness of several to dozens micron. In those years, new processing techniques such as nanotechnology have provided more choices for sensors manufacturing technology and the development of processing techniques also motivates the breakthrough of sensor technology.

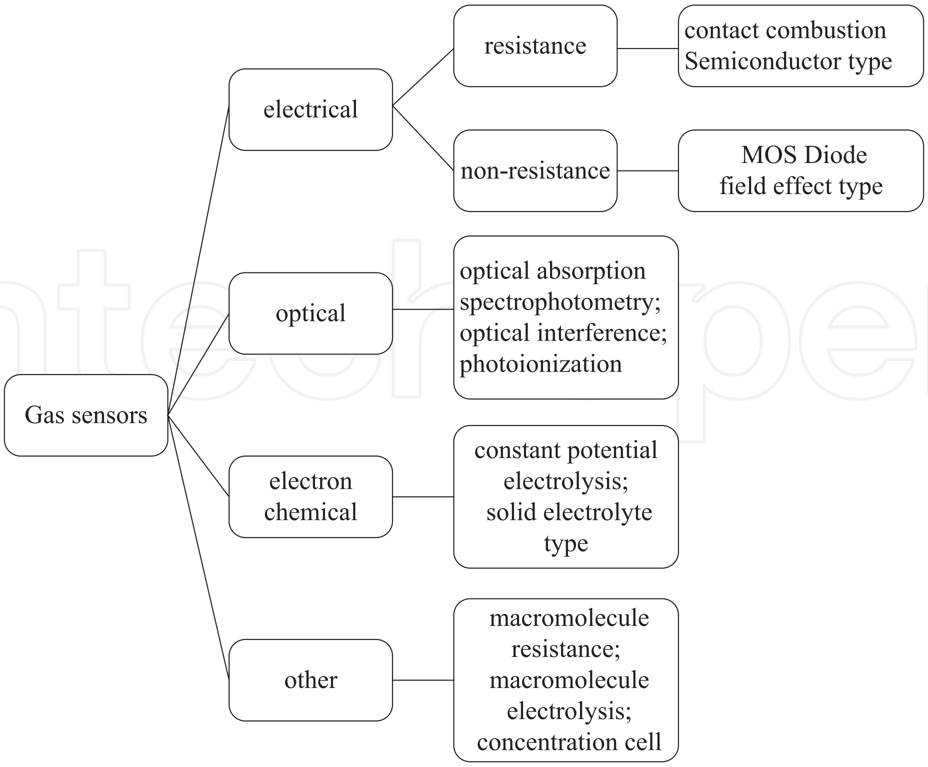


**Figure 1.** Classification chart of gas sensors.

| Detectors | Advantages | Disadvantages |
|---|---|---|
| Field-effect tube detector | Only for $H_2$ detection, no interference by other gases | Not long lifespan, severe zero drift, false alarm |
| Catalysis incendiary detector [37] | Low cost, long lifespan, low effect by temperature and humidity, high-speed response, widely used for $H_2$, $CH_4$ detection | Not suitable for other gases, low gas selectivity |
| Semiconductor detector [38, 39] | By far the most widely used sensors, high response value, high response speed, good stability | Low gas selectivity |
| Combustion cell detector | Often used for $H_2$ detection, high detection precision, good repeat response capability | Limited lifespan, high cost and detection error |
| Infrared absorption detector | Often used for $CO_2$ detection, no sample separation | For useable for other gases |
| Optical gas sensor [40–42] | Electromagnetic insulation properties, high response speed, high response value, long lifespan, good stability | Complex detection system, high cost |
| Electrochemical gas sensor [43–45] | High response value, good gas selectivity | Easy influence from outside environment |
| High polymer gas sensor [46] | High response value to specific gases, good gas selectivity, important in food production | Only works under common temperature |

**Table 2.** Comparison of the use features of common detectors.

### 2.2. Development status of CNTs-based gas sensors

Nowadays, with the development of industry manufacturing, environment detection as well as nanotechnology, nanogas-sensing technology has become the research focus of sensing technology. The development of nanotechnology provides not only excellent gas-sensing materials such as nanoparticles, nanowire, and nanoplane, but also new preparation and processing technology like scanning tunneling microscopy (STM) which enables researchers to observe the atoms and handle these atoms using probe. Therefore, this technology has developed a lot in biology, chemistry, machine, aviation, etc. Another important aspect of nanogas-sensing technology is CNTs gas sensors.

Since Iijima [47] found CNTs in 1991, both physical and chemical properties have been investigated widely. CNTs can be seen as tubes with nanosizes by graphite flake rolling. Hexagonal structural carbon atoms constitute several to 10 layers of tubes, with the distance between interfacing layers of 0.34 nm. There are single-wall CNTs (SWNT) and multi-wall CNTs (MWNT) according to the layers of CNTs as shown in **Figure 2**. The external diameter of CNTs is about several to dozens of nanometers and the length is about micron, much longer than the diameter.

CNTs possess abundant pore structure, large specific surface area, and excellent adsorption and desorption ability to gas molecules. Due to the interaction of adsorbed gas molecules with CNTs, the fermi level of it will change, thus leading to large macroscopic change of its resistance, which provides a way to detect the gases by the measurement of resistance. Those properties enable CNTs huge advantages as gas sensors. Firstly, large interaction surface provides gas adsorption sites with gas-sensing response enhanced largely. Secondly, working temperature can be lowered largely. Thirdly, gas sensors can also be controlled at very small size.

In recent years, considerable researches on CNTs sensors have been carrying on for the exploration of novel sensing materials. In 2000, Kong et al. [48] first applied the SWCNT to prepare gas sensors for detecting the mixture of $NO_2$ and $NH_3$, and they found that the conductivity of sensors after adsorbing $NH_3$ can reduce two orders of magnitudes and improve three orders of magnitudes in terms of $NO_2$. In that case, the sensors can be regarded as having a relatively

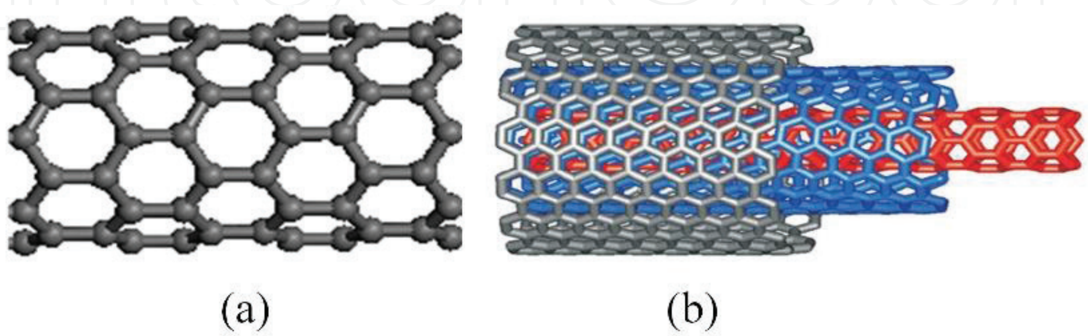


**Figure 2.** Structure sketch of CNTs: (a) single-wall nanotubes, (b) multi-wall nanotubes.

high selectivity in complex gas environment. Subsequently, Kong et al. [49] successfully prepared the N-modified SWCNTs with inconsecutive Pt metal thin film, which has better sensing property and quicker recovery property to $H_2$, demonstrating that this semi-conductivity single-wall CNTs sensors have better sensitivity, selectivity, and recovery characteristics than before. Dai et al. [6] developed a novel type of CNTs sensors, which were also made by SWCNT that have the semi-conductivity property, and they studied the change of electric property with the import of gases. The results showed that the gas responses of $NO_2$ and $NH_3$ are both good. Qi et al. [50] introduced a type of gas sensors using SWCNTs, which can detect $NO_2$ with the minimum content to 1 ppb.

Varghese et al. [51] proposed two kinds of means to prepare CNTs sensors. The first one is to cover a layer of CNTs-$SiO_2$ thin film on the flat interdigital capacitor, named capacitance sensor; the other one is to carve a crooked $SiO_2$ groove on a Si substrate and then to grow CNTs on the $SiO_2$, called resistive transducer. It has been proved that these two types of sensors are both sensitive to $NH_3$, presenting the liner change. Modi et al. [52] employed CNTs arrays and developed micro gas-sensing device using Thompson discharge characteristic that can sensitively detect the content of atmosphere gases.

Robinson et al. [53] of the America Marine laboratory designed a capacitance gas sensor based on CNTs, where the interdigital electrodes and the SWCNT that distributes in the interdigital electrodes are acted as a counter electrode of the capacitance, the 30nm $SiO_2$ layer acted as insulating layer between two poles, low-resistance silicon acted as another counter electrode. The experimental results showed that these sensors have quick response and short recovery time to $NO_2$, $NH_3$, and dimethyl methylphosphonate (DMMP). Pulichel M. hjayan and Nikhil Koratkar in Rensselaer Polytechnic Institute successfully developed the micro gas-sensing samples, which can sensitively quantify and qualitatively analyze varying gases in the atmosphere.

When implementing direct voltage on the gas sensors, the low voltage would generate strong electric field on the CNTs, and therefore form the dielectric breakdown condition. The experimental results reveal that the voltage values vary obviously with the difference of the type of gas, so that it can be qualitatively analyzed. The analyzable gases are extensive, ranging from Ar to He as well as some inert gases. Furthermore, it has been proved that the generated electricity values present direct proportion to the logarithm of the concentrations, which indicates the gas content could be quantitatively analyzed.

Zhang et al. [54] of Xi'an Jiaotong University as well as Bondavalliet al. [55] had performed an in-deep research to Thompson discharge type CNTs gas sensor. Xi Li also conducted primary study on CNTs film sensors. Zhang et al. [56] of Chongqing University also performed related studies on the electric properties of CNTs.

In terms of sensing mechanism of CNTs, many calculations based on first principle theory have been carried out. Goldoni et al. [57] deemed that the reasons SWCNTs are sensitive to $O_2$, CO, $H_2O$, and $N_2$ could be attributed to the combined induction of surfactant, lauryl sodium sulfate and contaminant come from NaOH, or the chemical adsorption between the defect zone of the CNTs and $O_2$.

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Jing Li [58] considered that two sensing mechanisms are existed in the adsorption process of SWCNTs: (i) the direct charge transfer between single-wall CNTs and the acceptor or receptor, inducing the change of semi-conductivity CNTs in Femi energy, which further results in the change in conductivity, named in-tube adjust and (ii) inside the SWCNT existing the adsorption points between targeted molecules and SWCNT, leading to the charge transfer, contributing to the change of conductivity, named inter-tube adjust.

Zhou et al. [59] who applied density functional theory calculated the effect of B- and N-doped SWCNT on adsorption to H atom and $H_2$ molecules. Owing to the complexity of porous materials and diversity of doping substance of CNTs, the gas-sensing mechanism of CNTs still remains in qualitative or half qualitative stage, which also needs further studies both experimental and theoretical.

To improve the sensitivity and selectivity of the CNTs sensors, a large number of modified methods such as chemical doped, molecules doped, molecular coating, as well as mechanical deformation [60–69] were introduced by scholars to modify the CNT, and acquired the desirable results. The variety of chemical doped and doped materials contributes to the selectivity to various gas adsorption. For example, the B-doped and N-doped make the intrinsic CNTs become P-model and N-model semiconductor, improving the density of the carrier so that make the charge transforms much easier between gas molecules and CNTs. Through doping Au, Pt, Pd, Ir, and the other expensive metal nanoparticles, the activation energy of chemical adsorption for gases can be reduced; at the same time, these expensive metal nanoparticles become the core of the catalytic activity, so that can effectively enhance the sensitivity, selectivity, and response time of the sensors.

## 3. Theoretical analysis of modified CNTs-based gas sensor

### 3.1. Gas-sensing properties of CNTs-OH gas sensor

#### *3.1.1. Calculation details*

The simulation of quantum mechanics is realized by the $Dmol^3$ of Material Studio software, which is developed by an American company of Accelrys. The PW91 function of the generalized gradient approximation (GGA) was employed for the exchange correlation of electrons. P polarized function is used for modified hydroxyl (OH)-wall (8, 0) SWNT in presence of gas molecule adsorption density functional calculations. Previous theoretical calculations [70] show that the generalized gradient approximation (GGA) method can accurately describe the geometric structure and electronic structure of CNTs, and the process of interaction with molecules. To avoid the interaction between the nanotubes, we designed a large lattice of 20 Å × 20 Å × 85 Å, and use the periodic boundary conditions. In a superlattice, the SWNT-OH is made up with 64 C atoms and the -OH which modified in the sidewall of CNTs. The initial action distance between gas dissolved in oil-filled transform and SWNT-OH can be set to 0.15 nm. All atoms are calculated by the atomic potential, self-consistent field convergence value is set to 10 × $10^{-5}$. Literature [70] shows we can get more accurate calculation results on CNTs (8, 0) brillouin zone 2 K points. All the calculation procedures completed on the Dmol[3].

Before each calculation, the first stage is to optimize the SWNT-OH of the superlattice and the isolated typical dissolved gases to get their stable configuration. And CO, $H_2$, $CH_4$ $C_2H_4$, and $C_2H_2$ are chosen as the typical dissolved gases to be detected by SWNT-OH in this part. Then let the CO, $H_2$, $CH_4$, $C_2H_4$, and $C_2H_2$ molecule in various passible ways, respectively, to approach the O and H atom of the -OH of the tube wall to make atomic optimization, and form the oil-dissolved gases molecule SWNT-OH system preliminarily. Finally, this system is unconstrained optimized to find the stable configuration and calculate its electronic properties.

*3.1.2. Calculate results*

In **Figure 3**, it is the SWNT-OH stable configuration after geometry optimization. In **Figure 4(a)–(e)**, they are CO, $C_2H_2$, $H_2$, $CH_4$, and $C_2H_4$ stable configuration after geometry optimization. And in **Table 3**, is the calculation results of SWNT-OH respectively absorb the CO, $H_2$, $CH_4$, $C_2H_4$, and $C_2H_2$. In **Figure 5**, are the most stable configuration of after interaction between the geometrically optimized gas molecules and SWNT-OH. The unit of structure parameter is Å. The brackets correspond to adsorption energy which unit is eV. The charge transfers $Q_T$ between oil-dissolved gases molecule and SWNT-OH are shown in **Table 3**.

In order to determine the most stable geometry configuration of the system of oil-dissolved gases molecule and SWNT-OH, we designed the different initial configuration. In other words, let the different atoms of CO, $H_2$, $CH_4$, $C_2H_4$, and $C_2H_2$ molecule with the same ini-

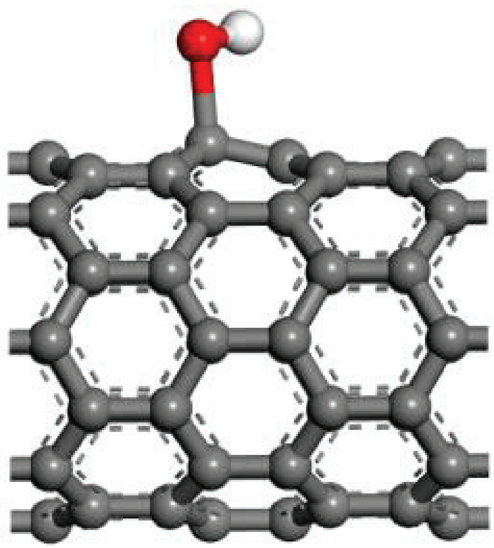

**Figure 3.** (8, 0) SWNT-OH.

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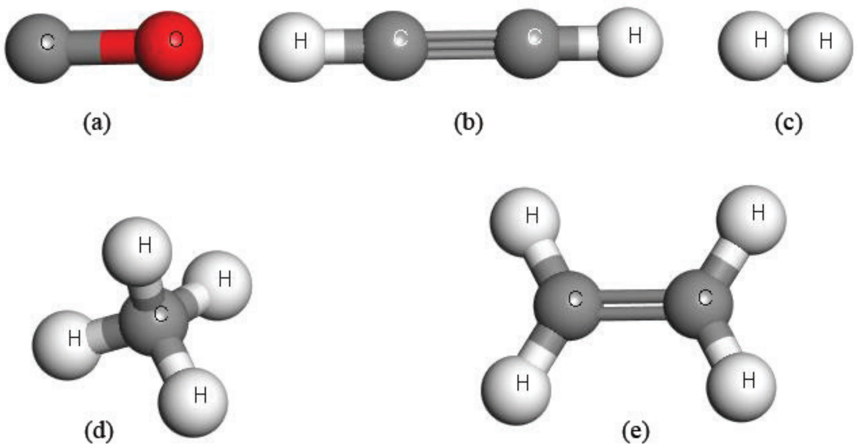


**Figure 4.** Optimized supercell structures for (a) CO, (b) $C_2H_2$, (c) $H_2$, (d) $CH_4$, and (e) $C_2H_4$.

tial distance (1.5) approach the O and H atom of -OH to optimize. And in order to evaluate the adsorption energy between molecules and SWNT-OH, we calculated their adsorption energy $E_b$. $E_b$ is defined as $E_b = E_{(B + SWNT\text{-}OH)} - E_{(SWNT\text{-}OH)} - E_{(B)}$. In this formula, $E_{(B + SWNT\text{-}OH)}$ is the total energy of molecular adsorption on the surface of SWNT-OH; $E_{(SWNT\text{-}OH)}$ and $E_{(B)}$, respectively, are the energy of SWNT-OH and single molecule. If $E < 0$, the adsorption process is an exothermic process, the adsorption can be occurred spontaneously. In order to characterize the electrical conductivity of SWNT-OH, we calculated the charge transfers $Q_T$ between molecule and SWNT-OH. The amount of charge transfer is able to provide the important information of the electronic response of the system. QT is defined as the charge transfer between SWNT-OH and single molecule [71].

As shown in **Table 3**, all of adsorption energy between CNT-OH and each oil-dissolved gas molecules are less than 0.6 eV. Therefore, the interaction between CNTs-OH and each oil-dissolved gas molecules is physisorption because chemisorption energy should be larger than 0.6 eV. As shown in **Figure 5** and **Table 3**, the value of charge transfer between CO and CNTs-OH (0.052 au) is nearly six times the value of that between $H_2$ and CNTs-OH (0.012 au) though

| Structural system | Graphic | Adsorption energy (eV) | Charge-transfer (au) | Interacting distance (nm) |
|---|---|---|---|---|
| $H_2$ + SWNT-OH | **Figure 5(a)** | −0.25 | 0.012 | 0.2211 |
| CO + SWNT-OH | **Figure 5(b)** | −0.22 | 0.062 | 0.2159 |
| $CH_4$ + SWNT-OH | **Figure 5(c)** | −0.36 | 0.017 | 0.2409 |
| $C_2H_4$ + SWNT-OH | **Figure 5(d)** | −0.49 | 0.052 | 0.2413 |
| $C_2H_2$ + SWNT-OH | **Figure 5(e)** | −0.59 | 0.068 | 0.2409 |

**Table 3.** Calculated binding energy, net charge transfer, and interacting distance.

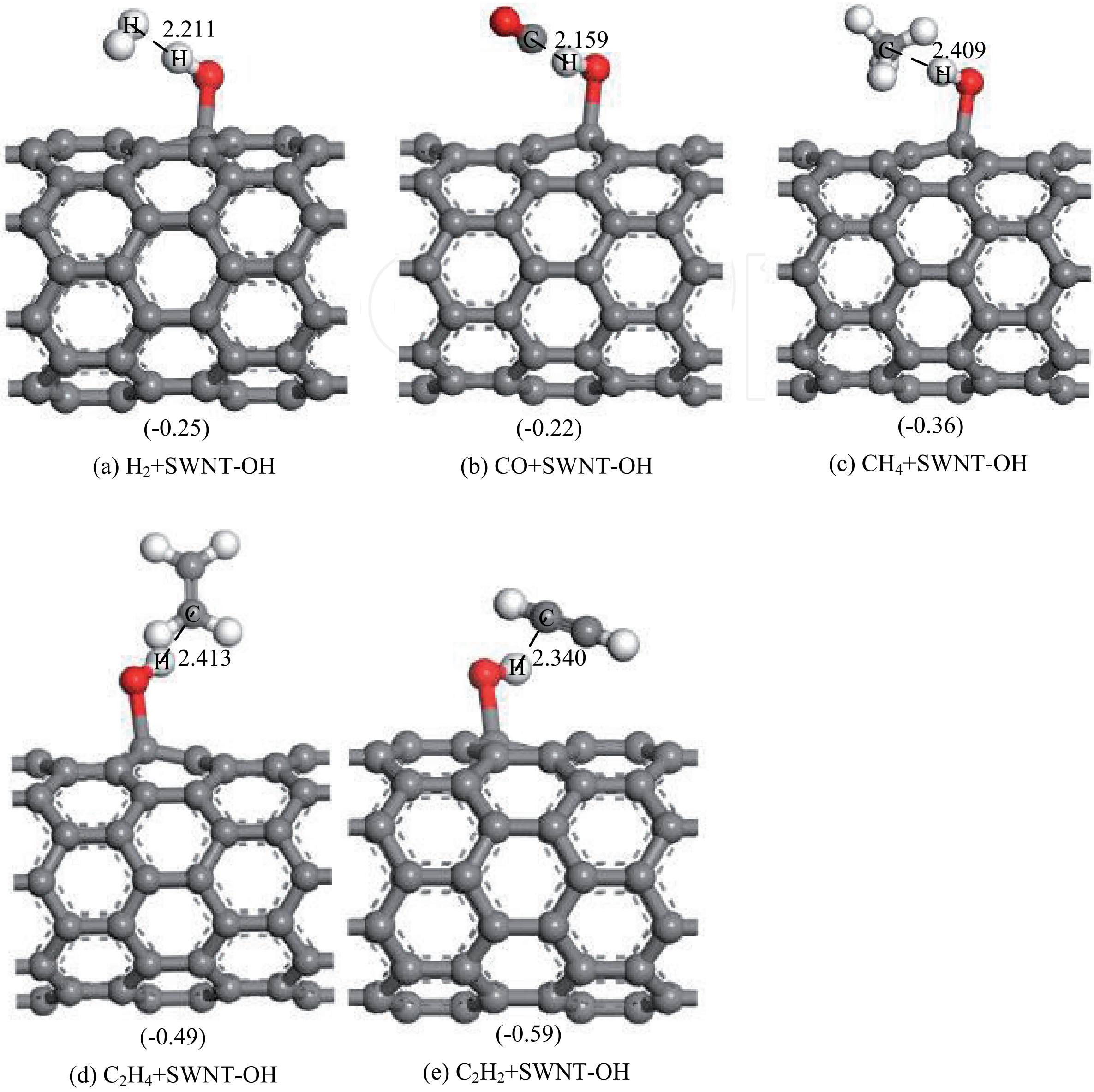


**Figure 5.** The most stable configurations of $H_2$, CO, $C_2H_4$, and $C_2H_2$ interacting with SWNT-OH after optimization, respectively.

the interaction distance and adsorption energy between $H_2$ and CO and CNTs-OH are almost the same. Then CNTs-OH can be used to detect CO due to the strong sensitivity if there is no organic gas in oil-dissolved gas molecules. Comparing with inorganic gas, the average adsorption energy between organic gas ($CH_4$, $C_2H_4$, $C_2H_2$) is about 0.48 eV, which is two times the average adsorption energy (0.23 eV) between inorganic gas (CO, $H_2$) and CNTs-OH. In addition, the charge transfer (0.046 au) between organic gas and SWNT-OH is far more than that between the inorganic gas value (0.037 au) between inorganic gas and SWNT-OH. This is because the hydroxyl modification on the surface of SWNT enhances its interaction to organic gas molecules due to the activation of hydroxyl. Thus, SWNT-OH is more sensitive to organic gas in oil. If we only consider the organic gas: $CH_4$, $C_2H_4$, and $C_2H_2$, the adsorption

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energy decreases in order: $C_2H_2$ (0.59 eV) > $C_2H_4$ (0.49 eV) > $CH_4$ (0.36 eV), and charge transfer decreases in order: $C_2H_2$ (0.068 au) > $C_2H_4$ (0.052 au) > $CH_4$ (0.017 au) as shown in **Table 3**. With the increase of C—C covalent, it leads to the increase of adsorption energy, resulting in the high sensitivity to $C_2H_2$. Hence, CNTs-OH can be used to detect $C_2H_2$ component in oil-dissolved transformer.

In order to evaluate the influence of oil-dissolved gas to the change of conductivity during the adsorption process, density of states (DOS) is calculated as shown in **Figure 6**. On comparing the calculation results shown in **Figure 6(a)–(f)**, gas adsorption narrows down the DOS at fermi level. Upon inorganic gas: $H_2$ and CO adsorption shown in **Figure 5(b)** and **(c)**, it is found that the energy gap of DOS around fermi level for CO + CNTs-OH is smother and narrower than that of $H_2$ + CNTs-OH adsorption system, signifying the increase of conductivity after CO adsorption. The result is also in consistence with the results that the charge transfer in CO + CNTs-OH system is larger than that of $H_2$ + CNTs-OH. Upon organic gas: $CH_4$, $C_2H_4$, and $C_2H_2$ adsorption shown in **Figure 6(d)–(f)**, the DOS of organic gas molecules adsorbed SWNT-OH system at fermi level is greater than that of inorganic adsorbed SWNT-OH system, indicating the strong interaction between organic gas molecules and SWNT-OH comparing with that of inorganic adsorption, which is also consistence with the results in **Table 3**. And the DOS for $C_2H_2$ + CNTs-OH system around at fermi level is obviously larger than that of other gas adsorption systems, thus SWNT-OH is most sensitive to $C_2H_2$ gas. Therefore, SWNT-OH can be used to detect $C_2H_2$ in oil-filled transformer.

#### *3.1.3. Conclusion*

In this study, density functional theory has been used to study the adsorption properties of hydroxyl-modified CNTs (CNTs-OH) upon gases dissolved in oil-filled transformer. According to the calculation results of first-principles calculations, the adsorptions to all of the gases are physisorption, which leads to the change of geometric and electronic structures. The adsorption energy to organic gases is bigger than inorganic gases, especially reflecting in the great adsorption energy to $C_2H_2$. Therefore, we conclude that SWN-OH can be chosen as gas sensor to detect $C_2H_2$ gas dissolved in oil-filled transformer.

### 3.2. Gas-sensing properties of Ni-CNTs gas sensor

#### *3.2.1. Calculations details*

The results showed that different oil-dissolved gases have different responses on the Ni-CNT sensor. To further understand the sensing mechanism, we established a properly simplified model to calculate and analyze the adsorption properties of the supports (CNTs and Ni-CNTs) to the gases. Ni-substituted CNTs and typical oil-dissolved gases were constructed to simulate the sensor in this part. $C_2H_2$, $C_2H_4$, and $C_2H_6$ are chosen as the target measured gases due to the specific sensitivity and selectivity of Ni-CNT sensor.

Totally optimized geometries and related properties of the configurations were carried out by Design for Testability (DFT) calculations in the generalized gradient approximation using the

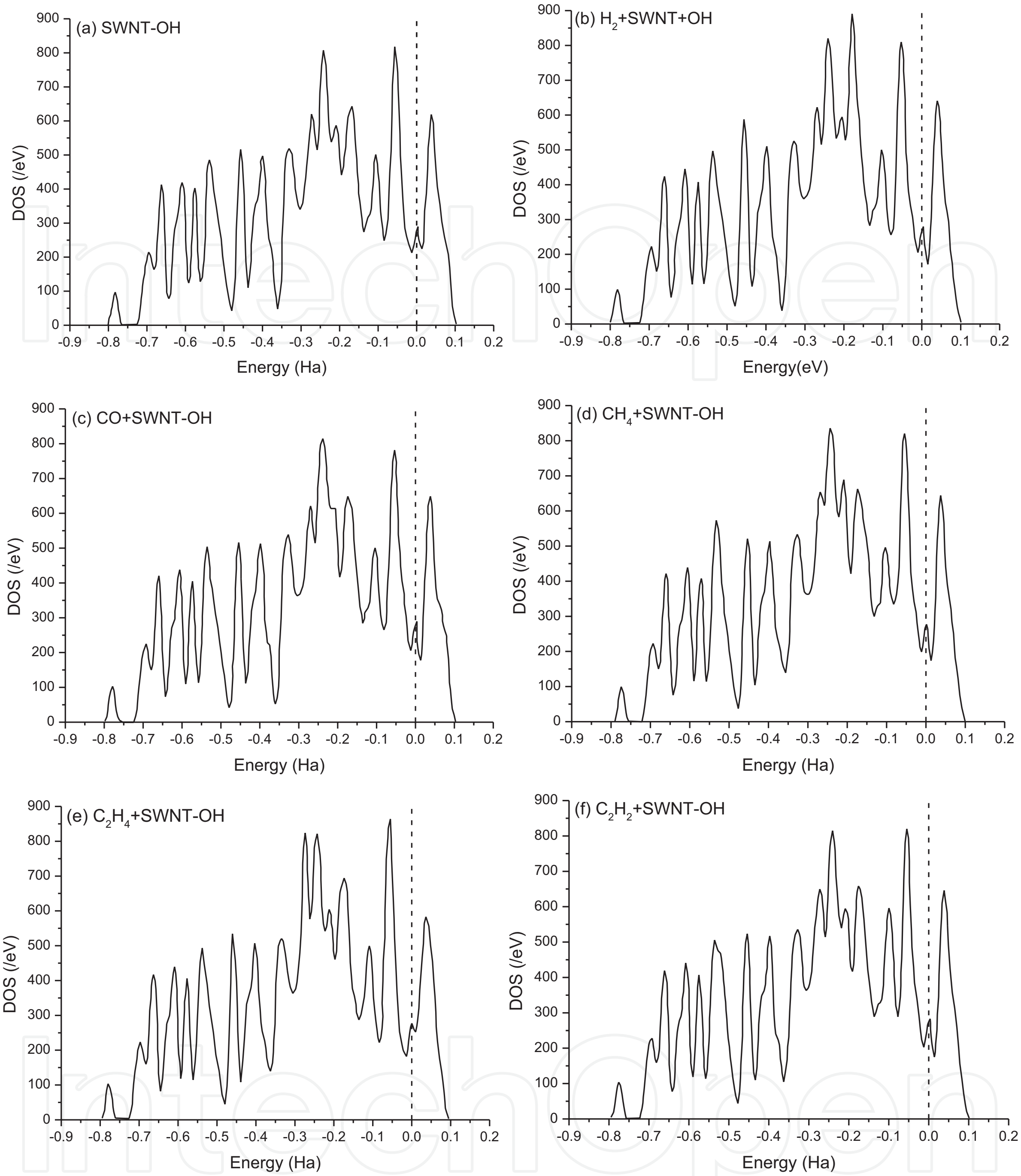


**Figure 6.** Calculated density of states for SWNT-OH, $H_2$ + SWNT-OH, CO + SWNT-OH, $CH_4$ + SWNT-OH, $C_2H_4$ + SWNT-OH, $C_2H_2$ + SWNT-OH.

Dmol$^3$ model with double-numerical polarized basis sets. The whole calculations were performed using the Perdew-Burke-Ernzerhof (PBE) DFT. The geometrical structures are shown in **Figures 7** and **8**.

### *3.2.2. Results and discussion*

The spontaneity of these interactions can be described by the adsorption energy $E_{ads}$, which is defined as follows:

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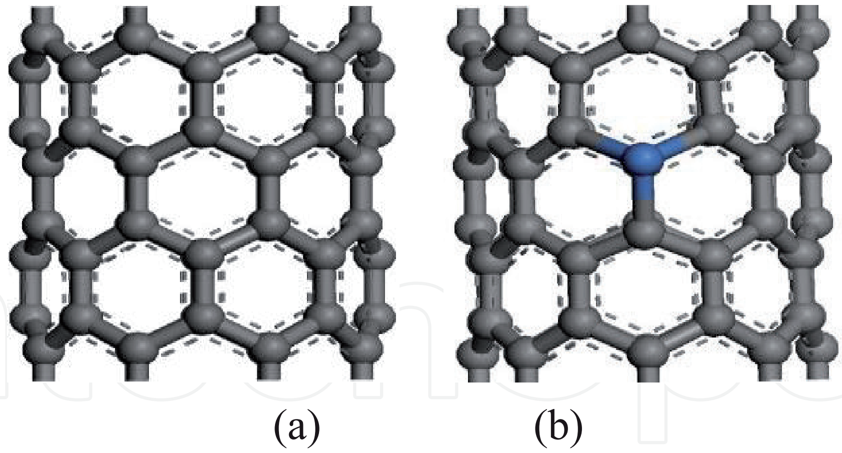

Figure 7. Geometrical structures of CNTs and Ni-CNTs. (a) CNTs, (b) Ni-CNTs.

$$E_{ads} = E_{(gas/support)} - E_{(support)} - E_{(gas)} \quad (1)$$

where $E_{(gas/support)}$ is total energy of adsorbed system after adsorption of gas molecule, $E_{(support)}$ is the energy of support without gas molecules adsorption, $E_{(gas)}$ is the energy of individual gas molecule. $E_{ads} < 0$ represents that adsorption process is exothermic and spontaneous.

Mulliken population of gas molecules and support were calculated, respectively, so that the charge distribution of the system can be obtained in the adsorption process. Charge transfers $Q_T$ was defined as charge variation before and after adsorption of gas molecules. The values of adsorption energies were negative showed that the adsorption was exothermic. And in this CNT system, the values of the energy were small (<0.6eV), and as follow order: $C_2H_2 > C_2H_4 > C_2H_6$. The charge transfers close to zero show that the adsorptions of gas molecules on the surface of CNTs are physisorption. And the sensitivity of adsorption is as follows: $C_2H_2 > C_2H_4 > C_2H_6$.

**Table 4** shows the adsorption energy and charge transfers of the Ni-CNT system and the CNT system. Compared with the CNT system, the doped Ni effectively improved the electronic structure and sensitivities of CNTs. The adsorption energies of $C_2H_6$ are the lowest, and $C_2H_2$ and $C_2H_4$ are 8.7 and 4.6 times larger than that of $C_2H_6$, respectively. The values of charge transfers of three gases are as follows: $C_2H_2 > C_2H_4 > C_2H_6$. Both the adsorption energies and charge transfers of $C_2H_2$ are highest. Thus, Ni-CNTs have the highest sensitivity to $C_2H_2$, which is similar to that of the CNTs.

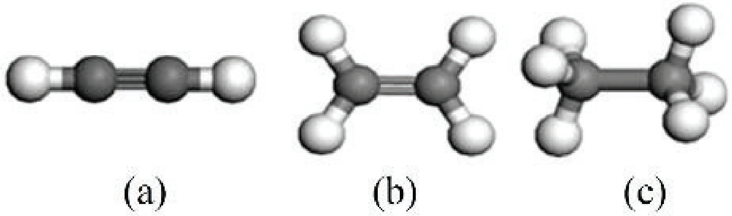

Figure 8. Geometrical structures of oil-dissolved gases (a) $C_2H_2$, (b) $C_2H_4$, (c) $C_2H_6$.

| | $E_{ads}$ (eV) | $Q_T$ (e) |
|---|---|---|
| $C_2H_2$-CNTs | −0.3265 | 0.006 |
| $C_2H_4$-CNTs | −0.2814 | 0.003 |
| $C_2H_6$-CNTs | −0.0458 | 0.002 |
| $C_2H_2$-Ni-CNTs | −1.7412 | 0.091 |
| $C_2H_4$-Ni-CNTs | −0.9246 | 0.069 |
| $C_2H_6$-Ni-CNTs | −0.1994 | 0.043 |

**Table 4.** Adsorption energy and charge transfer.

In summary, the sensitivity of the CNT sensor for the gases is as follows: $C_2H_2 > C_2H_4 > C_2H_6$, and the doped Ni can improve the sensor sensitivity.

The molecular orbit theory was calculated to obtain the highest occupied molecular orbital (HOMO) energy and the lowest unoccupied molecular orbital (LUMO) energy of the three gas molecules and the supports. The analysis of HOMO and LUMO and related energy gap are able to determine whether charges can easily transform between gases and adsorbent or not. $E_{L\text{-}H}$ is calculated based on the following equation:

$$E_{L\text{-}H} = E_{LUMO} - E_{HOMO} \tag{2}$$

A small $E_{L\text{-}H}$ corresponds to an easy transferred charges between the orbitals and to a good conductivity for this material. The calculated $E_{HOMO}$, $E_{LUMO}$, and $E_{L\text{-}H}$ are depicted in **Table 5**. The $E_{L\text{-}H}$ of CNTs and Ni-CNTs are 0.6911 and 0.5470 eV, respectively. The Ni dopant reduces the $E_{L\text{-}H}$ of 0.1441 eV so that enhances the conductivity of the carbon nanotube. After adsorption, the frontier orbital energies of the adsorption configurations are increased and $E_{L\text{-}H}$ changed as well, their values are in order as follows: $C_2H_2$-Ni-CNTs < $C_2H_4$-Ni-CNTs < $C_2H_6$-Ni-CNTs. Therefore, conductivities of adsorbent in the adsorption systems are in order as follows: $C_2H_2$-Ni-CNTs > $C_2H_4$-Ni-CNTs > $C_2H_6$-Ni-CNTs.

In the process of Ni-CNTs adsorption, the conductivity change of the adsorption system shows that $C_2H_2$ is the highest, while $C_2H_6$ is the lowest. The change of resistance shows

| Adsorption type | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | $E_{L\text{-}H}$ (eV) |
|---|---|---|---|
| CNTs | −4.5606 | −3.8695 | 0.6911 |
| Ni-CNTs | −4.9797 | −4.4327 | 0.5470 |
| $C_2H_2$-Ni-CNTs | −4.5906 | −4.1606 | 0.4300 |
| $C_2H_4$-Ni-CNTs | −4.6940 | −4.2477 | 0.4463 |
| $C_2H_6$-Ni-CNTs | −4.7593 | −4.1933 | 0.5660 |

**Table 5.** Molecular frontier orbital energy and orbital energy differences.

the same changing characteristics. This result indicates that the sensitivity of Ni-CNTs is as follows: $C_2H_2 > C_2H_4 > C_2H_6$. This finding is consistent with the results based on gas-sensing experiments.

*3.2.3. Analysis of theoretical calculate*

In this chapter, to detect oil-dissolved gases in a transformer, the research's work includes theoretical and experimental studies on a Ni-CNT sensor. This study focuses on the response and mechanism of gas sensing. The results of gas-sensing experiment are consistent with the simulation.

Charge redistribution between the surface and the adsorbed molecules results in changes in the electronic structure and conductivity. Higher charge transfer results in greater conductivity changes. The values of transfer charges calculated based on DFT are shown in **Table 4**. Compare with other two gases, the transfer charges of $C_2H_2$ are the highest, and $C_2H_2$ has the highest response on the gas sensor. In addition, the orbital theory results are consistent with the charge transfer analysis and experimental results. Thus, in this chapter, the theoretical analysis results are consistent with the experimental results, and the sensitivities of the three gases on Ni-CNTs are as follows: $C_2H_2 > C_2H_4 > C_2H_6$. Moreover, as the $C_2H_2$ concentration increases, the response time becomes shorter. High gases concentration leads to fast sensor response.

Previous researches signified that gas-sensing properties can be enhanced by metal doping. The transition metal is rich in d-electrons and has empty orbits, and the small gas molecules can be strongly combined with the metal when adsorbed on the surface. In this chapter, nickel ions are the transition metal divalent cations used, which make nickel ions more accessible to the internal tubes in the capillary. Moreover, due to the coordination unsaturation of the surface atoms of nickel ions, the surface active sites of CNT increase and the catalytic activity is greatly enhanced. In general, the order of the chemical adsorption capacity of the transition metal to the gas is as follows: $O_2 > C_2H_2 > C_2H_4 > CO > H_2 > CO_2 > N_2$. The results of this paper are consistent with this order, which indicating that the doped Ni increases the chemical adsorption of the gas molecules.

*3.2.4. Conclusion*

**a.** The adsorption between three gases and intrinsic CNTs is physical adsorption, and the order of adsorption sensitivity is as follows: $C_2H_2 > C_2H_4 > C_2H_6$.

**b.** The adsorption sensitivity of the Ni-CNTs was consistent with that of the CNTs, doping Ni improves the conductivity of the CNT, and the adsorption of the three gases becomes easier on Ni-CNTs.

**c.** Due to the coordination unsaturation of the surface atoms of nickel ions, the surface activity sites of CNTs increase and the catalytic activity is greatly improved. Doped Ni improves the ability of the tube to adsorb gas molecules.

**d.** When a low concentration (1–10 μL/L) of $C_2H_2$ is detected, the relative change in sensor resistance $R$% and gas concentration satisfies a certain linear relationship, indicating that the developed sensor can detect low gas concentrations.

## 4. Experimental analysis of modified CNTs-based gas sensor

### 4.1. Preparation of CNTs sensors

#### *4.1.1. Arc discharge method*

It is the first and most used method to prepare CNTs. The main processes are: (a) keep a certain pressure of inert gas or hydrogen in vacuum vessel and (b) choose graphite (with catalyst: nickel, cobalt and iron, etc.) as electrode. The graphite is consumed by evaporation at anode during the arc discharge process, and CNTs are received by depositing at cathode. Ebbsen and Ajayan [72] successfully prepared gram order weight of CNTs under nitrogen gas condition, and then this method is widely adopted. In 1994, Bethune introduced catalyst for arc reaction, reducing the reaction temperature and enhancing the productivity of CNTs. In 1997, Journet et al. [73] used catalysts for synthesizing single CNTs under helium condition. Mingliang et al. [74] studied the influence factors to CNTs prepared by DC arc discharge method: (a) inert gas pressure will affect the diameter and length of CNTs. (b) How much the adhesion of particles? (c) Oxygen and water vapor will lead to defects in CNTs, and it is unable to separate and purify after sintering together. (d) Current and voltage will affect the yield and production rate of CNTs, but length to diameter ratio of graphite does not affect the generation of CNTs.

#### *4.1.2. Catalytic cracking method*

Catalytic cracking method, also known as chemical vapor deposition, prepares CNTs through cracking hydrocarbons or carbon oxides with the help of catalyst. The basic preparation processes are: (a) mix the organic gases (such as acetylene and ethylene) with certain proportion of nitrogen gas in quartz tube. (b) CNTs grow on the surface of catalyst under certain temperature when the carbon source flow past and pyrolysis onto the surface of catalyst, and pushing forward the small catalyst particles [75]. (c) The growth of CNTs ends till all of the catalyst particles were coated with graphite layer. The advantages of the method are: easy to control the reaction process, simple equipment, low raw material cost, easy to produce the product in large scale, and the high productivity. The disadvantages are: too much CNTs layers, poor graphitization, exist crystalline defects. Theses disadvantages have great adverse influence on the physical and chemical properties of CNTs.

#### *4.1.3. Laser evaporation method*

Laser evaporation method prepares CNTs by illuminating the graphite target that contain metal catalyst. Then the vapor mix with carbon source and deposit on the surface of substrate and the wall of reaction chamber. Smalley et al. received SWCNTs after adding a certain amount of catalyst to the electrode during preparing $C_{60}$. After improving the method, Thess et al. [76] successfully fabricated amount of SWCNTs. Under the condition of 1473 K, the graphite target with Ni/Co catalyst particles was irradiated by double pulse laser with 50 ns, receiving the high quality SWCNTs bundles.

#### *4.1.4. Low temperature solid state pyrolysis method*

Low temperature solid state pyrolysis prepares CNTs through intermediate. First, the nanometer level silicon nitride ($Si_2C_2N$) ceramic intermediate was prepared. The nanoceramic intermediate is then placed in a boron nitride crucible, which is heated in a graphite resistance furnace to decompose it with nitrogen gas as the protective gas. After 1 h, the nanointermediate powder begins to paralyze, and the carbon atoms migrate to the surface. A high proportion of CNTs is obtained with amount of silicon nitride powder in the surface pyrolysis products. The advantage of the low temperature solid state pyrolysis method is the repeatable production, which is beneficial for large-scale CNTs production.

#### *4.1.5. Polymer pyrolysis method*

The method prepares CNTs by decomposition of hydrocarbons precursor (such as acetylene and benzene) at high temperature. Cho et al. [70] prepared CNTs by heating the polymer obtained from citric acid and glycol after polyesterification under 400°C for 8 hours. The CNTs were synthesized by using metal Ni as catalyst in the temperature ranged from 420 to 450°C and under $H_2$ atmosphere. Under the 900°C and Ar-$H_2$ atmosphere conditions, Sen et al. [77] obtained CNTs by pyrolyzing ferrocene, nickelocene, and cobaltocene. These metal compounds not only provide carbon source after pyrolysis but also provide the catalyst particles. The growth mechanism of the method is similar to the catalytic cracking method.

#### *4.1.6. Ion (electron beam) radiation method*

In a vacuum furnace, carbon is evaporated by ion or electron discharge and deposit on the condenser. Chernozatonskii et al. [78] synthesized CNTs with diameter range from 10 to 20 nm and high alignment by evaporating the graphite coated on the surface of substrates. Yamamoto et al. [79] got CNTs with diameter range from 10 to 15 nm by irradiating amorphous carbon with argon ion beam under high-vacuum environment [80].

#### *4.1.7. Flame synthesis method*

Flame synthesis method utilizes the heat, produced by burning methane and a small amount of oxygen, and imports hydrocarbons and catalysts at temperature of 600–1300°C to synthesize CNTs. The CNTs prepared by this method have the disadvantages of low crystallinity and large amount of amorphous carbon. There is still no definite explanation for the growth mechanism of CNTs nanostructure by flame method. Richter et al. [81] found SWCNTs that attached with a large amount of amorphous carbon from carbon black after burning the mixture of acetylene, oxygen, and argon gases. Das Chowdhury et al. [82] found nanometer tubular CNTs by detecting carbon black after burning the mixture of benzene, acetylene, ethylene, and oxygen gases.

#### *4.1.8. Solar energy synthesis method*

The CNTs are received from the condensation of high temperature (3000 K) mixture vapor of graphite and metal catalyst that heated by focusing the sunlight. This method is initially used for buckyballs production, then adopted for CNTs synthesis since 1996. Laplaze et al. [83] synthesized that the CNTs and SWCNTs use this method.

#### *4.1.9. Electrolysis method*

The preparation of CNTs by electrochemical method is a novel technique. This method adopted graphite electrode (electrolytic cell as anode) and obtained carbon nanomaterials by electrolyzing molten alkali halide salts (such as LiCl) under a certain voltage and current with the protection of air or argon gases at about 600°C. The products include packaged or not packaged CNTs and carbon nanoparticles, and the form of carbon nanomaterials can be controlled by changing the process conditions of electrolysis. Goldoni et al. [57] found that CNTs can directly grow on the surface of n type of (1 0 0) silicon electrode in solution of acetylene/ammonia. Hsu et al. [84] synthesized nanotubular and onion-like CNTs under argon environment by using molten alkali metal halide as electrolyte and graphite as electrode. Hui et al. [85] successfully synthesized CNTs and carbon nanowires using LiCl and LiCl + $SnCl_2$ as molten salt electrolyte.

#### *4.1.10. Other methods*

Stevens et al. [86] got CNTs by using an exothermic reaction between cesium and nanoporous amorphous carbon in the low temperature of 50°C. Chernozatonskii et al. [87] found the fullerene and CNTs at the micro holes of $Fe_2Ni_2C$, $Ni_2Fe_2C$, and $Fe_2Ni_2Co_2C$ alloy prepared by powder metallurgy method [88]. Kyotani et al. [89] first pyrolyze and deposit carbon on the wall of anodic alumina model (with nanometer trench) under 800°C. Then hollow CNTs with open-end on both sides after removing the anodic alumina membrane by hydrofluoric acid. Matveev et al. [90] synthesized CNTs using liquid nitrogen solution of acetylene at 233 K by electrochemical method. It is the lowest temperature ever reported to synthesize CNTs.

### 4.2. Gas-sensing properties of mixed acid-modified CNTs gas sensor

#### *4.2.1. Sample preparation*

This chapter used CNTs which were made by chemical vapor deposition method. Tube diameter is 20–30 nm, with a length of 10–30 μm, purity > 95%, the catalyst residue (ash) < 1.5 wt%, and multi-walled structure. Around 0.1 g of CNTs was placed in an appropriate amount of anhydrous ethanol, then adding surface active agent. Afterward, it had been scattered by ultrasonic oscillator with 2 hours in order to obtain a moderate concentration of CNTs solution, which was set as the sample I. Similarly, another 0.1 g of CNTs was immersed in 50 mL mixed acid solution, which was initially prepared by mixing concentrated sulfuric acid and concentrated nitric acid with the volume ratio of 3:1. The solution was put in ultrasonic oscillator for about 2 hours of dispersion. And then the solution was diluted with deionized water, and filtrated by filter membrane with an aperture of 0.22 μm. This progress should be conducted repeatedly until the diluted solution becomes neutral. The finally collected sample is named as sample II.

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*4.2.2. Sensor preparation*

The printed circuit board was used to make the substrate of CNTs sensors. The surface of substrate was etched by copper to generate interdigital electrodes. Copper foil has the thick of 30 μm, with 0.5 mm electrode interval and 0.5 mm line width, as shown in **Figure 9**.

Once moderate concentration solution of the sample I was obtained, the micro-scale parts were spread on the space between the interdigital electrodes, and then placed in a drying oven at 80°C to dry it. Uniform dense of MWNTs film with smooth surface was able to be prepared with repeated operations. The obtained sample is named as the sensor I, as shown in **Figure 9(b)**. Take appropriate sample II placed in anhydrous ethanol, and then after ultrasonic dispersion for 10 min to get moderate concentration of the suspension. Sensor II was obtained in the same way. These two-dimensional CNTs films generated from the deposition of the one-dimensional CNTs have so many structural defects, making it possess specificity of electrical properties.

*4.2.3. Detection of dissolved gases in oil test using MWNTs sensor*

Device for detection of dissolved gas in transformer oil by CNTs-based sensors is shown in **Figure 10**. Prepared CNTs sensors were initially placed in the test device. It was a sealed chamber

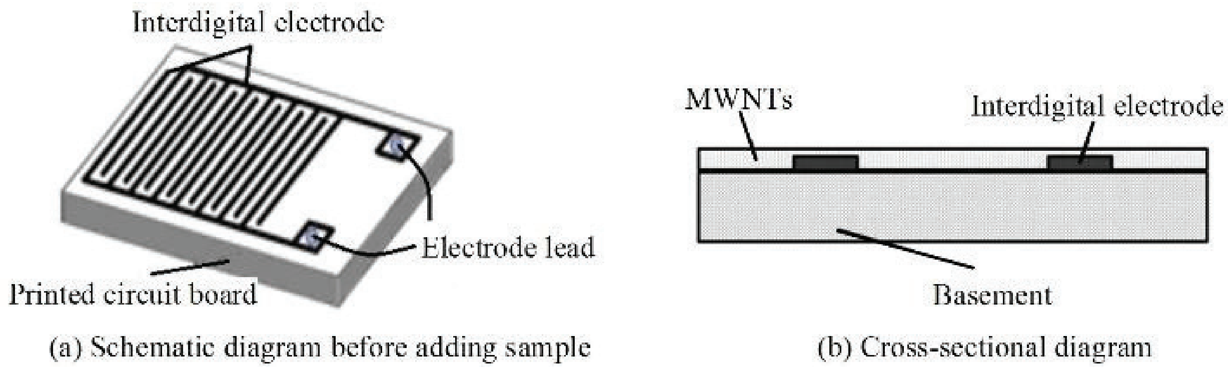


**Figure 9.** The geometric sketch of CNTs sensor.

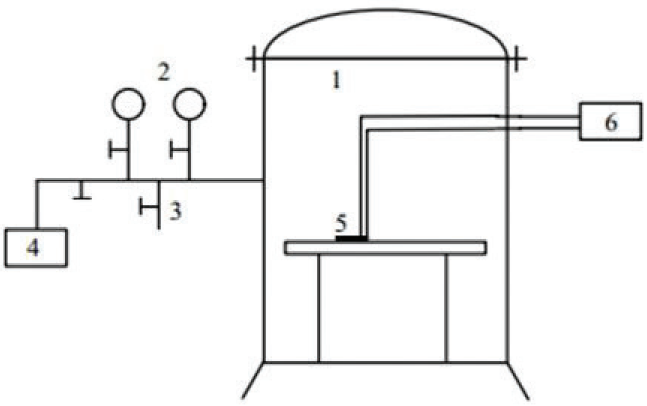


**Figure 10.** Detection test device for the CNTs sensor adsorbing gases dissolved in transformer oil. 1: sealed metal can, 2: vacuum gauge and pressure gauge, 3: intake valve, 4: vacuum pump, 5: CNTs sensors, 6: impedance analyzer.

designed to perform this experiment. Then the sensor was connected with the impedance analyzer by wire and the chamber was then sealed with a round head passing through the spherical ring with a screw and a nut.

The standard gas of $CH_4$ with concentration of 200 μL/L is injected through the intake valve into the test device, as shown in **Figure 10**, and use sensors I and II to detect gas response, respectively. The acquired gas response curves are shown in **Figure 11**. Based on **Figure 11**, *S*% indicates the relative change of resistance, *R* is the sensor resistance value after the interaction with injected gas, and $R_0$ is the resistance of the sensors in a vacuum environment.

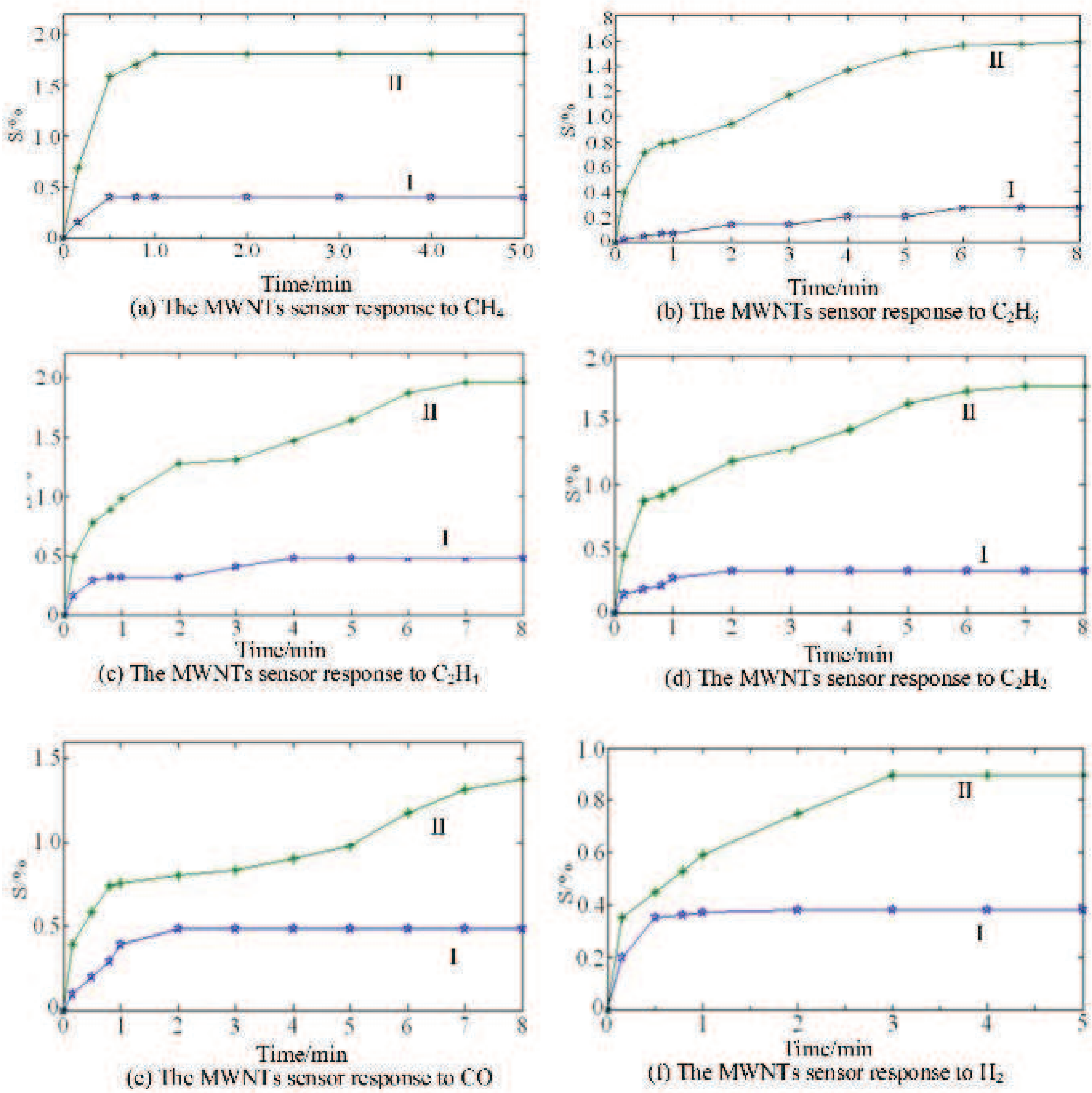


**Figure 11.** The MWNTs sensor response to $CH_4$, $C_2H_6$, $C_2H_4$, $C_2H_2$, CO, $H_2$.

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In **Figure 11(a)**, curves I and II show response curve of sensors I and II, respectively. It can be observed that the changes of MWNTs thin-film sensor in resistance value are very small without chemical modification, about 0.4%; while the one conducted with chemical modification has great change with respect to resistance value, reaching to 1.8%.

After detection, a vacuum pump is used to make the device vacuumed again, according to the same method. Inject $C_2H_6$, $C_2H_4$, $C_2H_2$, CO, and $H_2$ gas into the tank, respectively, with concentration of 200 μL/L. Then detect the response curve using sensors I and II, respectively. Obtained response curves are shown in **Figure 11(b)–(f)**.

Combining **Figure 11(a)–(f)** obtains **Table 6**, the resistance value change of CNTs which had adsorb the measured gas and being chemically modified is much greater than that of the non-modified CNTs. After calculation, adsorption capacity of modified CNTs to $CH_4$, $C_2H_6$, $C_2H_4$, $C_2H_2$, CO, and $H_2$ increased by about 4.6, 5.9, 4.2, 5.3, 2.9, and 2.4 times, respectively. It can be seen that chemical modification contributes great affection upon the electrical properties of MWNTs.

The CNTs film is regarded as a connection of many disordered CNTs or CNTs, among which there are considerable series-parallel paths. The high-resistance samples contain more series path than parallel paths, while low-resistance samples on the opposite. Gas-adsorption property is closely related to charge transfer capacity, adsorption sites, and the characteristics of gas molecules as well. Adsorption sites of gas molecules in carbon nanotubes include: the tube gaps of a bundle of CNTs, the grooves on the surface of the bundle between tubes, the inner cavity of CNTs as well as the tube surface. Recently, many researchers agree that there are two kinds of carriers in CNTs, electrons and holes, Cantalini et al. [91] and some other scholars argue that the MWNTs is a P-type semiconductor properties, namely the electron would be accepted by gas molecules after adsorption of oxidation substances, so that concentration of holes would be increased, and resistance value would be decreased; on the other hand, once reducing gases are adsorbed on the CNTs surface, their electrical resistance increases. Given that in oil, methane and other gases have certain reducibility, it can result in an increase in electrical resistance after their adsorption on CNTs surface. As analyzed, if the carbon nanotubes are pretreated with concentrated nitric acid and concentrated sulfuric acid, its length would be shortened, ports be opened, and a lot of depressions on the surface

| **Gas (200 μL/L)** | **The relative change in resistance value (%)** | |
|---|---|---|
| | **I** | **II** |
| $CH_4$ | 0.39 | 1.81 |
| $C_2H_6$ | 0.27 | 1.60 |
| $C_2H_4$ | 0.47 | 1.96 |
| $C_2H_2$ | 0.33 | 1.76 |
| CO | 0.48 | 1.38 |
| $H_2$ | 0.38 | 0.90 |

**Table 6.** Relative changes of CNTs resistance value to different gases in oil.

as well as at ports be generated. Then a large number of stable functional groups such as carboxyl, hydroxyl, and carbonyl are bonded to the adsorbing sites of depression, which would increase the number of active sites for gas adsorption, contributing to better gas sensitivity.

#### *4.2.4. Conclusion*

CNTs-based gas sensors that have advantages of high sensitivity, fast response, and small size can work at room temperature. This chapter took good use of these electrical properties, introduced a multi-walled CNTs gas sensor. Laboratory mixed acid modification was employed to improve the gas-sensing properties of CNTs to dissolve gases in transformer. Results show that without modification, MWNTs sensors are insensitive to dissolved gas in transformer oil; while the modified MWNTs sensor that has many faults and contains active functional groups guarantee the good sensitivity and fast response characteristics to the dissolved gas in oil. Synthesis of CNTs sensors industrially and large-scaly to realize this purpose is hard, but it provides a novel way for this detection. In the further work, researches should focus on gas-sensing response mechanism, sensitivity, and selectivity of so-prepared CNTs. It is hopeful and promising to prepare CNTs-based sensors that have better performance for detection of dissolved gas in oil.

### 4.3. Gas-sensing properties of Ni-CNTs gas sensor

Due to the low growth temperature, and the atmospheric pressure during the reaction, etc., the Chemical Vapor Deposition (CVD) is widely used in the synthesis of CNTs. The sensitivity of the sensor to typical oil-dissolved gases was studied. $C_2H_2$, $C_2H_4$, and $C_2H_6$ are chosen as the target measured gases in consistence with theoretical calculation above.

#### *4.3.1. Preparation of the Ni-CNT sensor*

In this chapter, the purity of the CNTs is more than 95%, which diameter and length are ranged from 20 to 30 nm and 10 to 30 μm, respectively. At first, a mixed solution of concentrated sulfuric acid (98%) and nitric acid (78%) at a concentration ratio of 3:1 was arranged, then put into 0.1 g CNTs, and dispersed in an ultrasonic shaker for 60 min. Second, washed several times with deionized water until the solution became neutral and then dried at 70°C. After these two steps, the dark powder of the mixed acid-modified CNTs can be obtained.

To prepare 1 mg/mL solutions of CNTs, take appropriate amount of CNTs dissolved in anhydrous ethanol. Take 20 mg $NiCl_26H_2O$ dissolved in 50 mL 1 mg/mL solutions of CNTs. In order to obtain a uniform dispersed Ni-CNTs solution, put the beaker in an ultrasonic bath for 90 min. Using coating drops prepared the Ni-CNTs thin films on the surface of interdigital electrodes and dried at 80°C. To ensure a compact and smooth distribution of the sensing film, repeated this process.

#### *4.3.2. Sensor response experiment*

The device for detecting the gas-sensing properties is shown in **Figure 12**. The main part of the device is a steel chamber that is sealed by screws. Before the test, the pressure tightness of the device should be examined and guaranteed.

http://dx.doi.org/10.5772/intechopen.68590

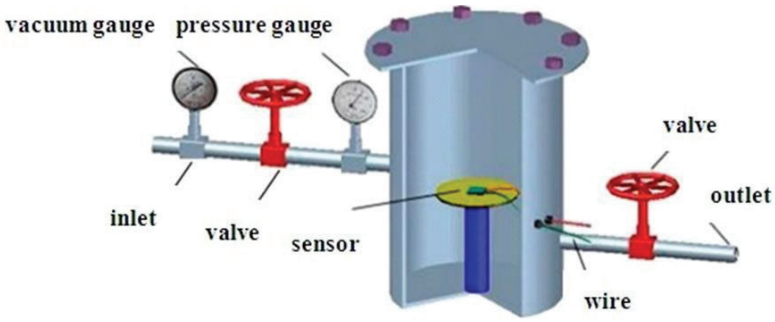


**Figure 12.** Geometry of the experimental equipment.

First, the sensor was put inside the chamber and connected with an impedance analyzer through wires to record the measured resistance. Second, nitrogen was passed through the chamber until the resistance of the sensor becomes stabilized. Then, different concentrations of the target gas species were injected into the sealed chamber through the inlet valve. The relative variation of the resistance was calculated as expressed:

$$R\% = (R - R_0)/R \times 100\% \tag{3}$$

where $R$ is the sensor resistance in relevant gas and $R_0$ is the sensor resistance in the environment full of nitrogen. After each test, the chamber should be evacuated for the next test. All the operations in this work were performed at room temperature.

*4.3.3. Experiment result and discussion*

The gas responses of the Ni-CNTs prepared gas sensor upon the concentrations of 10 μL/L $C_2H_2$, $C_2H_4$, and $C_2H_6$ were detected using the method described above. The gas response curves are shown in **Figure 13**, where the horizontal axis represents time, and the vertical axis represents resistance. In order to avoid accidental factors that affect the detection results, data presented here are the results of statistical analysis preformed on 10 sensor samples instead

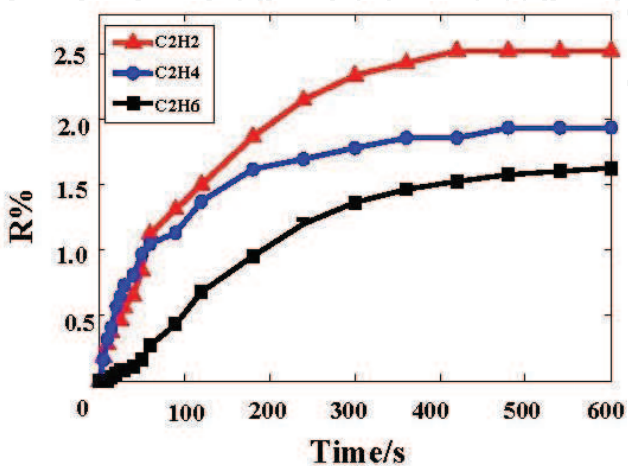


**Figure 13.** Ni-CNT sensor response to 10 μL/L $C_2H_2$, $C_2H_4$, and $C_2H_6$.

of one set. The gas sensitivity in this work is an average value. The calculated standard deviations of $C_2H_2$, $C_2H_4$, and $C_2H_6$ are 0.0374, 0.0288, 0.0275, respectively (data not shown).

**Figure 13** shows that there is a sharp rise in the resistance of the Ni-CNT-based sensor at first when exposed to atmosphere filled with $C_2H_2$, $C_2H_4$, and $C_2H_6$, and then becomes stable after 400 s. It can be observed that the relative variations of the resistance for $C_2H_2$, $C_2H_4$, and $C_2H_6$ are nearly unchanged at 2.52, 1.95, and 1.61%, respectively. These results indicate that the Ni-CNTs sensor presents the most sensitivity to $C_2H_2$ under the same concentration compared with the other two gases.

#### *4.3.4. Gas response of Ni-CNT upon different $C_2H_2$ concentrations*

A standard value of the dissolved gas in the transformer oil is 5 μL/L. In order to meet the engineering requirements, the gas-sensitive response of $C_2H_2$ at concentrations of 1, 3, 5, and 10 μL/L were all tested, with related result shown in **Figure 14(a)**. The change of prepared sensors in resistance to 1, 3, 5, and 10 μL/L $C_2H_2$ are obtained as 0.52, 1.05, 1.18, and 2.52%, respectively. With the increasing concentration, the relevant change in resistance increases as well, and the response time is accordingly shortened. **Figure 14(b)** depicts the linear fit curve of the response and gas concentrations with the linear correlation coefficient ($R^2$) of 0.98. These results imply that when the $C_2H_2$ concentration is between 1 and 10 μL/L, the change of Ni-modified CNT in resistance meets a certain linear dependence with the gas concentration, which indicates that this material can be applied to estimate the concentration of $C_2H_2$ gas.

#### *4.3.5. Reproducibility of Ni-modified CNTs*

The sensor reliability is strongly depended on the reproducibility that is exhibited by the sensor material. The reproducibility of the Ni-doped CNTs sensor was evaluated by repeating the response experiments for three times. Tests were conducted according to the experimental steps described in Section 2.2. Pure $N_2$ was employed to accelerate desorption of gas molecules. The dynamic response transients for the Ni-doped CNTs sensors toward 10 μL/L $C_2H_2$ gas is depicted in **Figure 15** in order to illustrate desorption and repeatability processes. Based

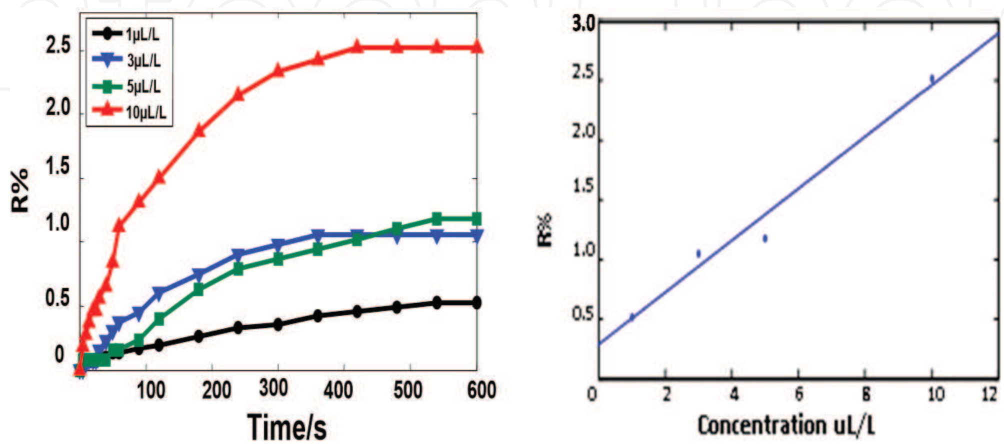


**Figure 14.** The gas response of Ni-CNTs sensors to different concentrations of $C_2H_2$. (a) Gas response curve to different concentrations of $C_2H_2$, (b) liner fitting curve.

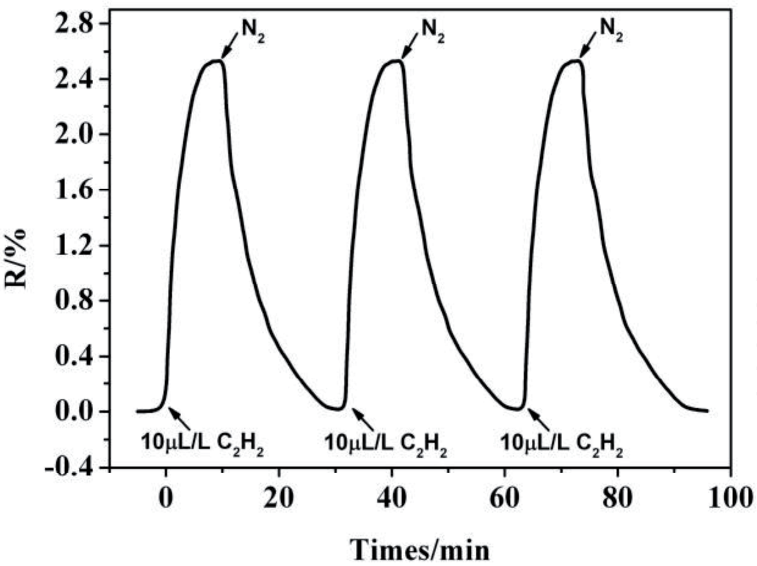


**Figure 15.** Reproducibility of Ni-doped CNTs sensor to 10 μL/L $C_2H_2$.

on this figure, one can find that the response of the material is almost constant, confirming the reproducibility of sensor material, which suggests that the Ni-CNTs-prepared sensor can be applied as a reusable sensing material for detecting oil-dissolved gases.

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