

Article

A Ni-Doped Carbon Nanotube Sensor for Detecting Oil-Dissolved Gases in Transformers

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Abstract: C₂H₂, C₂H₄, and C₂H₆ are important oil-dissolved gases in power transformers. Detection of the composition and content of oil-dissolved gases in transformers is very significant in the diagnosis and assessment of the state of transformer operations. The commonly used oil-gas analysis methods have many disadvantages, so this paper proposes a Ni-doped carbon nanotube (Ni-CNT) gas sensor to effectively detect oil-dissolved gases in a transformer. The gas-sensing properties of the sensor to C₂H₂, C₂H₄, and C₂H₆ were studied using the test device. Based on the density functional theory (DFT) the adsorption behaviors of the three gases on intrinsic carbon nanotubes (CNTs) and Ni-CNTs were calculated. The adsorption energy, charge transfer, and molecular frontier orbital of the adsorption system were also analyzed. Results showed that the sensitivity of the CNT sensor to the three kinds of gases was in the following order: C₂H₂ > C₂H₄ > C₂H₆. Moreover, the doped Ni improved the sensor response, and the sensor response and gas concentration have a good linear relationship.

Keywords: oil-dissolved gas; carbon nanotubes; nickel-doped; sensor response; linear relationship

1. Introduction

The special structures and properties of carbon nanotubes (CNTs) have attracted a great deal of attention of researchers at home and abroad since Iijima [1] introduced CNTs in 1991. CNTs have made a big difference in chemistry, physics, materials science, medicine, life sciences and other fields, which indicates that they have great potential application prospects [2,3].

CNTs are ideal materials for gas sensors because of their abundant pore structures, large surface-to-volume ratios, good conductivity and high surface activity. CNTs also exhibit strong adsorption and desorption capacity for gases [4–10]. Compared with traditional sensors, CNT gas sensors exhibit a fast response, high sensitivity, small size, and low working temperature [11,12]. Transformers are expensive and significant electric components in power transmission and distribution systems. Their safety and stable operation is critical to the whole power system. In long-term operation, local overheating, discharges, and insulation paper aging in an oil-immersed transformer, may produce a certain amount of gases that dissolve in the transformer oil. Among them C_2H_2 , C_2H_4 , and C_2H_6 are important components of the oil-dissolved gases. In order to effectively predict, detect and recognize the internal faults and latent failures in transformers, it is necessary to detect the composition and content of oil-dissolved gases generated by these faults [13–15].

Gas chromatography (GC) is an effectively detection method which can accurately determine the concentrations of different gases [15,16]. However, during long time operation the performance of chromatograph columns also degrades, so that regular maintenance and recalibration are needed. GC monitoring systems are also costly and must usually be used in the laboratory, so online monitoring cannot be performed. In order to know the running status and insulation level of transformers at any time, an online monitoring device is needed. Gas sensing detection technology is the core of an online monitoring device, which directly affects the accuracy and stability of on-line monitoring systems together with its service life. Metal oxide sensors have high working temperatures, long response times and poor selectivity which make them unsuitable for detecting oil dissolved gases [17,18]. Thus, a study on a CNT gas sensor for the three gases of interest is of vital significance.

In this paper, the response of a CNT sensor was investigated by both experimental and theoretical calculations. Results show that the adsorptions between the three kinds of gases and the intrinsic CNTs are all weak physisorptions. The Ni-doped CNTs (Ni-CNTs) sensors strengthen the adsorptions, and show improved sensor responses to C_2H_2 , C_2H_4 , and C_2H_6 .

2. Experimental Section

The CNTs used in this article were prepared using CVD, which is widely used in the synthesis of CNTs due to its many advantages such as low growth temperature, atmospheric pressure during the reaction process, low cost equipment and the production of products with high purity. The preparation method of the CNTs synthesis process and catalyst were similar to those described in [19]. Then a Ni-CNT gas sensor was developed. The sensing susceptibility of the sensor to C_2H_2 , C_2H_4 , and C_2H_6 was studied, and a plausible sensing mechanism was also analyzed.

2.1. Preparation of the Ni-CNT Sensor

The diameter of the CNTs used in this paper ranged from 20 nm to 30 nm, and their length ranged from 10 μm to 30 μm . The purity of the CNTs was more than 95%. Firstly, 0.1 g of CNTs was soaked in a 3:1 (v:v) solution of 98% sulfuric acid and 78% nitric acid, and then dispersed in an ultrasonic shaker for 60 min. Secondly, the solid phase was filtered and washed with deionized water several times until the solution became neutral, and then dried at 70 $^{\circ}\text{C}$. The dark powder obtained is the mixed acid-modified CNTs.

Taking appropriate amount of CNTs dissolved in anhydrous ethanol to prepare 1 mg/mL solutions. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (20 mg) was dissolved in 50 mL of 1 mg/mL CNT suspension, and then the beaker containing the CNTs and NiCl_2 was put in an ultrasonic bath for 90 min to obtain a uniform dispersed Ni-CNTs solution. Ni-CNTs thin films were prepared on the surface of interdigital electrodes (Figure 1) using coating drops and dried at 80 $^{\circ}\text{C}$. This process was repeated to ensure a compact and smooth distribution of the sensing film, as shown in Figure 1.

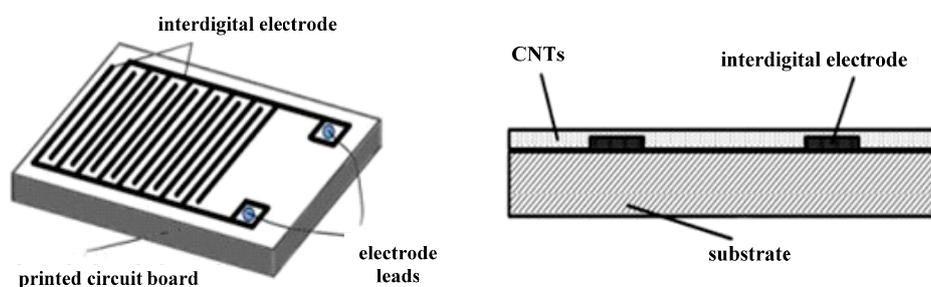


Figure 1. Sketch of the CNT sensor.

2.2. Sensor Response Experiment

The device for testing the gas-sensing properties is shown in Figure 2. The main part of the detection device is a steel chamber that is sealed by screws. Before the test, the pressure tightness of the device should be ensured.

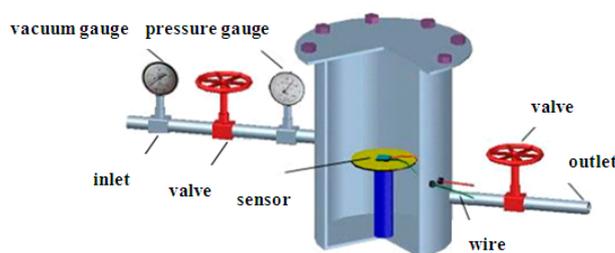


Figure 2. Schematic of the experimental setup.

First, the sensor was placed inside the chamber connected to an impedance analyzer through wires to record the changes in resistance, and then the cell was evacuated. Second, nitrogen gas was passed through the chamber until the resistance of the sensor stabilized. Then, different concentrations of the target gas species were passed into the sealed chamber through the inlet valve. The relative variation of the resistance was calculated as follows:

$$R\% = \frac{(R - R_0)}{R_0} \times 100\% \quad (1)$$

where R is the sensor resistance in relevant gas, and R_0 is the sensor resistance in nitrogen gas. After each test the chamber of the device should be evacuated for the next test. All the experiments in this paper were performed at room temperature.

2.3. Experiment Result and Discussion

The responses of the Ni-CNTs gas sensor for the concentrations of 10 $\mu\text{L/L}$ C_2H_2 , C_2H_4 , and C_2H_6 were tested using the method described above. The gas-sensitive response curves are shown in Figure 3, in which the horizontal axis represents time, while the vertical axis represents the change in resistance. In order to avoid accidental factors that affect the detection results, experimental results presented in this paper are the results of statistical analysis performed on ten sensor samples instead of one set. The gas sensitivity in this paper 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).

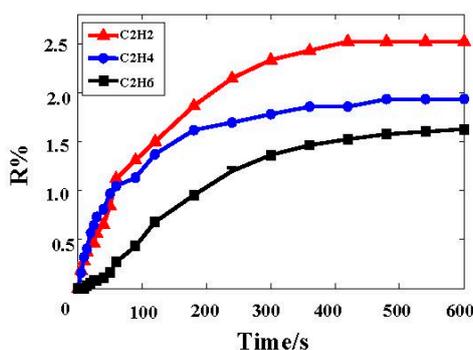


Figure 3. Ni-CNT sensor response to 10 $\mu\text{L/L}$ C_2H_2 , C_2H_4 , and C_2H_6 .

Figure 3 shows that there is a sudden increase in the resistance of the Ni-CNT sensor when exposed to C_2H_2 , C_2H_4 , and C_2H_6 at first, and then the resistance becomes stable. 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%, after 400 s. The results indicate that the Ni-CNTs sensor is most sensitive to C_2H_2 under the same concentration conditions compared with the other two kinds of gases.

2.4. Sensor Response of Different C_2H_2 Concentrations

A standard critical value of the oil-dissolved gas in the transformer is 5 $\mu\text{L/L}$ [20]. In order to meet the engineering requirements, the gas-sensitive response of C_2H_2 at concentrations of 1, 3, 5, and 10 $\mu\text{L/L}$ were tested. The result is shown in Figure 4a. The relative change values of the resistance to 1, 3, 5, and 10 $\mu\text{L/L}$ C_2H_2 are 0.52%, 1.05%, 1.18%, and 2.52%, respectively. With the increasing concentration, the relative change value of resistance increases, and the response time shortens. Figure 4b depicts the linear fit curve of the response and gas concentrations; the linear correlation coefficient R^2 is 0.98. The result indicates that when the C_2H_2 gas concentration is between 1 and

10 $\mu\text{L/L}$, the relative change value of resistance satisfies a certain linear relationship with the gas concentration, which can be used to estimate the concentration of C_2H_2 gas.

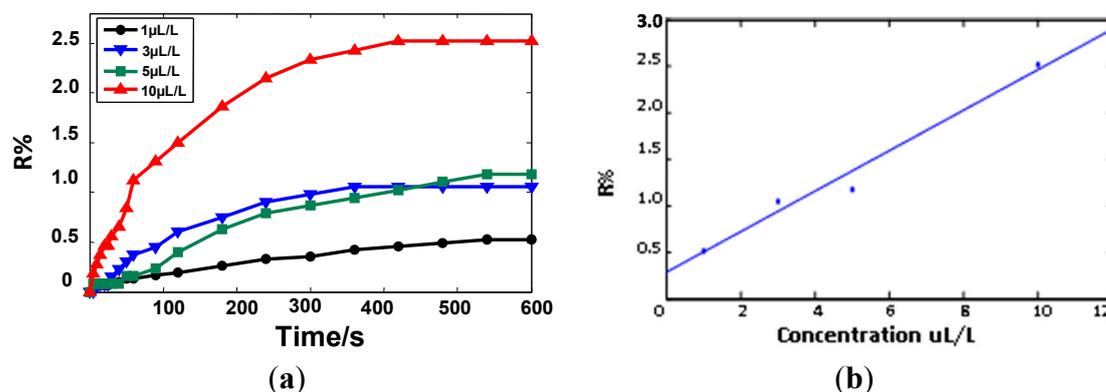


Figure 4. The gas-sensing properties of Ni-CNTs sensors to different concentrations of C_2H_2 . (a) Gas-sensitivity to different concentrations of C_2H_2 ; (b) Linear fitting curve.

2.5. Reproducibility of Ni-Doped CNTs

The sensor reliability is strongly dependent on the reproducibility exhibited by the sensor material. The reproducibility of the Ni-doped CNTs sensor was measured by repeating the response measurement three times. Tests were conducted according to the experimental steps described in Section 2.2. Pure N_2 was used to accelerate the desorption of gas molecules. Figure 5 depicts the dynamic response transients for the Ni-doped CNTs sensors towards 10 $\mu\text{L/L}$ C_2H_2 gas to illustrate the desorption and repeatability processes. Figure 5 shows that the response of the material is almost constant, confirming the reproducibility of sensor material. This suggests that the Ni-doped CNTs sensor can be used as a reusable sensing material for detecting oil-dissolved gases.

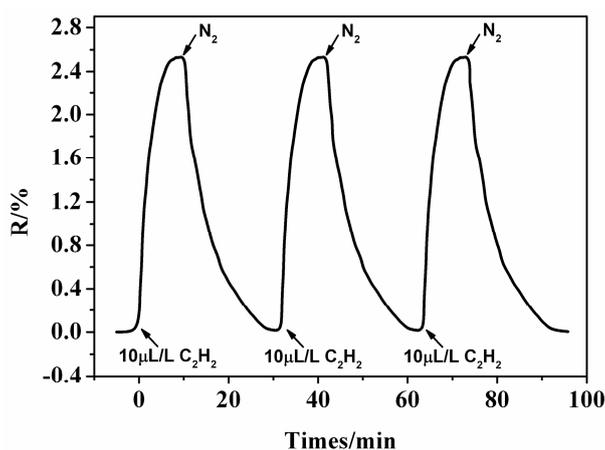


Figure 5. Reproducibility of Ni-doped CNTs sensor to 10 $\mu\text{L/L}$ C_2H_2 .

3. Theoretical Calculations

The experimental results showed that the Ni-CNT sensor has different responses to oil-dissolved gases. To further understanding the sensing mechanism, the adsorption properties of the supports

(CNTs and Ni-CNTs) to the gases were calculated and analyzed in a properly simplified model. Ni-substituted CNTs were constructed to simulate the sensor in our experiment.

3.1. Computational Details

Fully optimized geometries and the properties of the systems were derived by DFT calculations in the generalized gradient approximation by using the DMol³ code with double-numerical polarized basis sets. The calculations were performed using the PBE [21] DFT. The structural models are shown in Figures 6 and 7.

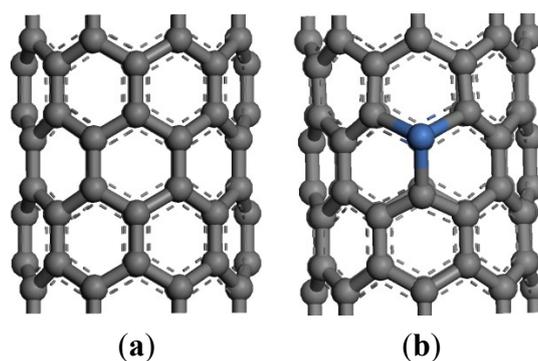


Figure 6. Structural model of CNTs and Ni-CNTs. (a) CNTs; (b) Ni-CNTs.

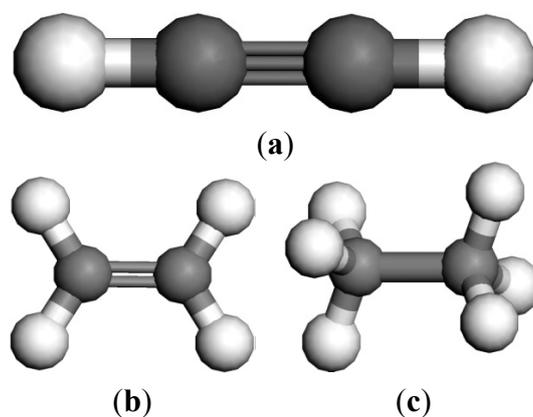


Figure 7. Structural model of oil-dissolved gases. (a) C₂H₂; (b) C₂H₄; (c) C₂H₆.

3.2. Results and Discussion

3.2.1. Adsorption Energy and Charge Transfer

The interaction can be described by the adsorption energy E_{ads} , which defined as follows:

$$E_{ads} = E_{(gas/support)} - E_{(support)} - E_{(gas)} \quad (2)$$

where $E_{(gas/support)}$ is the total energy of a gas molecule adsorbed on the support surface, and $E_{(support)}$ and $E_{(gas)}$ are the total energies of the support and the gas molecule. If $E_{ads} < 0$, the adsorption process is exothermic and spontaneous.

To obtain the charge distribution of the system, the charge transfer Q_T was calculated by Mulliken population analysis and define d as the charge variation of the isolated gas molecule after the

adsorption [22,23]. The adsorption energies are negative, which indicates that the adsorptions are exothermic.

In the CNT system: The values of the energy released in adsorptions are as follows: $C_2H_2 > C_2H_4 > C_2H_6$, all of them are small (<0.6 eV). In addition, the charge transfers are very small and close to zero, which indicates that the gas molecules are physisorbed and not chemisorbed on the surface of CNTs, and the van der Waals interaction between the gas and the support is weak. The sensitivity of adsorption is as follows: $C_2H_2 > C_2H_4 > C_2H_6$.

In the Ni-CNT system: Table 1 shows that both the adsorption energy and charge transfer of the Ni-CNT system are significantly increased compared with the CNT system. The doped Ni effectively improved the electronic structure and sensitivities of CNTs. The sensitivity of the sensor to three gases is consistent with that of the CNTs. The adsorption of C_2H_6 is the weakest, and the adsorption energies of C_2H_2 and C_2H_4 are 8.7 and 4.6 times that of C_2H_6 , respectively. The charge transfers of C_2H_2 and C_2H_4 are also higher than that of C_2H_6 . The charge transfer of C_2H_2 is the highest, and the adsorption energy of C_2H_2 is nearly two times that of C_2H_4 . Thus, Ni-CNTs have the highest sensitivity to C_2H_2 , which is similar to that of the CNTs.

Table 1. Adsorption energy and charge transfer.

	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

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.

3.2.2. Frontier Molecular Orbital Analysis

The highest occupied molecular orbital (HOMO) energy and the lowest unoccupied molecular orbital (LUMO) energy of the three gas molecules and the supports were calculated according to the molecular orbit theory [24,25]. An analysis of HOMO and LUMO can determine whether charges can easily transform between gases and supports or not. E_{L-H} is defined as follows:

$$E_{L-H} = E_{LUMO} - E_{HOMO} \quad (3)$$

If E_{L-H} is small, the energy charge needed to be transferred between the orbits is small, and the system with a good conductivity. The calculated E_{HOMO} , E_{LUMO} , and E_{L-H} are listed in Table 2.

The E_{L-H} of CNTs and Ni-CNTs are 0.6911 eV and 0.5470 eV, respectively. The doped Ni reduces the E_{L-H} of 0.1441 eV that enhances the conductivity of the tube. After adsorption, the frontier orbital energies of the adsorption systems increased and E_{L-H} also changed, there values are as followings: C_2H_2 -Ni-CNTs $<$ C_2H_4 -Ni-CNTs $<$ C_2H_6 -Ni-CNTs. Thus, conductivities of the adsorption systems are as follows: C_2H_2 -Ni-CNTs $>$ C_2H_4 -Ni-CNTs $>$ C_2H_6 -Ni-CNTs.

Table 2. Molecular frontier orbital energy and orbital energy differences.

	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{L-H} (eV)
CNTs	-4.5606	-3.8695	0.6911
Ni-CNTs	-4.9797	-4.4327	0.5470
C ₂ H ₂ -Ni-CNTs	-4.5906	-4.1606	0.4300
C ₂ H ₄ -Ni-CNTs	-4.6940	-4.2477	0.4463
C ₂ H ₆ -Ni-CNTs	-4.7593	-4.1933	0.5660

The conductivity change of the adsorption system in the process of Ni-CNTs absorbing C₂H₂ as well as the resistance change of the sensor sensing, C₂H₂ is the highest, while C₂H₆ is the lowest. This result indicates that the Ni-CNTs show the best sensitivity to C₂H₂ and the least sensitivity to C₂H₆. This finding is corresponding to gas sensing experiments.

4. Analysis of Experimental and Theoretical Results

In this paper, the research work includes theoretical and experimental studies on a Ni-CNT sensor for detecting oil-dissolved gases in a transformer. This research focuses on the gas-sensing response and mechanism. Gas sensing experimental results agreed with the simulation.

The gas molecules can be adsorbed on the surface of CNTs. Charge redistribution between the surfaces and the adsorbed molecules lead to changes in electronic structure and conductivity. A higher charge transfer results in a greater change in conductivity. The transfer charges calculated in this paper according to DFT are shown in Table 1. The transfer charges of C₂H₂ are the highest among these three gases, and the gas sensor showed the highest resistance variation to C₂H₂ (Figure 4). In addition, the orbital theory result coincides exactly with the charge transfer analysis and experimental results. Thus, in this paper, the theoretical analysis results are in agreement with the experiment results, and the sensitivities of Ni-CNTs to the three gases are as follows: C₂H₂ > C₂H₄ > C₂H₆. Besides, with increasing C₂H₂ concentration, the response time become shorter. The reason is that high gas concentrations can quickly adsorb on the surface of CNTs. In other words, adsorption rates improve in a shorter time.

Some studies have indicated that metal doping can effectively change the electronic structure and the conductivity of CNTs, therefore improving the gas sensing properties. Transition metals are d-electron rich and possess empty orbits, and the small gas molecules can bond strongly to the metal when adsorbed on the surface [26,27]. In this paper, nickel ions are the transition metal divalent cations used, which make nickel ions more accessible to the internal tubes in the capillary [28]. Besides, the surface active sites of the CNTs increase and the catalytic activity is greatly enhanced because of the coordination unsaturation of the nickel ion surface atoms. In general, the order of the chemical adsorption capacity of the transition metal to gas is as follows: O₂ > C₂H₂ > C₂H₄ > CO > H₂ > CO₂ > N₂. This order is consistent with the results of the article, namely, C₂H₂ > C₂H₄, which indicates that the doped Ni increases the chemical adsorption of the gas molecules. The adsorption of the gas molecules on the surface of the CNTs changed the surface barrier of the CNT gas-sensitive film, thereby significantly changing the electrical resistance of the sensor [5,29,30].

5. Conclusions

- (1) The gases C₂H₂, C₂H₄, and C₂H₆ can be physically adsorbed on intrinsic carbon nanotubes, and the adsorption sensitivity is as follows: C₂H₂ > C₂H₄ > C₂H₆.
- (2) Ni doped CNTs minimize the energy level difference and boost the conductivity of the CNTs. The adsorptions of the three gases became stronger, and the adsorption sensitivity of the Ni-CNTs was consistent with that of the CNTs.
- (3) The surface active sites of the CNTs increased and catalytic activity was greatly enhanced because of the coordination unsaturation of the nickel ion surface atoms. The doped Ni improved the ability of the tube to adsorb gas molecules.
- (4) When detecting low C₂H₂ concentrations (1 μL/L to 10 μL/L), the relative variation of the sensor resistance *R*% and the gas concentration meet a certain linear relationship, which indicates that the developed sensor can detect low gas concentrations.

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Author Contributions

Xiaoxing Zhang designed the experiments; Jia Lu wrote the manuscript; Xiaoqing Wu modified the manuscript; Ziqiang Dai performed the experiments and Jinbin Zhang did the simulation.

Conflicts of Interest

The authors declare no conflict of interest.

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