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The gas response of hydroxyl modified SWCNTs and carboxyl modified SWCNTs to H_2S and SO_2

***Abstract**. H_2S and SO_2 are important characteristic gases reflecting latent insulated defects in gas insulated switchgear (GIS).The detection of the H_2S and SO_2 is of great significance to diagnose and assess the operating status of GIS. In this paper, the single-walled carbon nanotubes (SWCNTs) are modified by hydroxyl and carboxyl, respectively. The gas sensing response of the modified SWCNTs to H_2S and SO_2 are studied. The results show that the sensitivity of SWCNTs modified by carboxyl is higher than that of SWCNTs modified by hydroxyl to H_2S, the same for SO_2.*

***Streszczenie.** Przedstawiono metodę detekcji H_2S iSO_2 jako możliwość oceny stanu izolacji przełączników gazowych GIS. Jako czujnik wykorzystano nanorurki węglowe SWCNTs modyfikowane przez wodorotlenki hydroxyl i carboxyl. (**Odpowiedź na obecność H_2S lub SO_2 czujników SWCNT modyfikowanych hydroxylem luv carboxylem**)*

Keywords: Carbon nanotubes, Functionalization, Gas sensor
Słowa kluczowe: nanorurki węglowe, czujniki gazu, przełączniki GIS

Introduction

Gas insulated switchgear (GIS) has been widely used in power systems due to its compact structure, small footprint and high reliability. However, there are some latent insulation faults which have inevitably emerged in the progress of manufacturing, assembly and operation of GIS, resulting in different degrees of partial discharge (PD) which leads to the decomposition of sulfur hexafluoride (SF_6) gas. It is well known that SOF_2, SO_2F_2, SOF_4, SO_2, H_2S, and HF are produced if there are trace amounts of air and water vapor. These gases are closely related to the degree and type of PD. H_2S and SO_2 are important characteristic gases of partial discharge produced by latent insulation defects in GIS[1]. Thus, the detection of H_2S and SO_2 has important significance in the diagnosis and assessment of the state of GIS equipment operations.

Gas sensor is one of the methods used in detecting the decomposition components of SF_6 under PD. Since it is found by Iijima[2], carbon nanotubes (CNTs) have received considerable attention as active elements for gas-sensing devices due to their rich hole structure and high surface to volume ratio; it is also characterized by conductance that can be easily perturbed by interaction with gas molecules. Compared with the conventional gas sensor, CNTs-based gas sensors present outstanding properties such as higher sensitivity, faster response, lower operating temperature, smaller size and a wider variety of detectable gas[3-10].

The intrinsic carbon nanotubes are only sensitive to a few gases such as NO_2, NH_3 and O_2, and the sensitivity to other gases is relatively low. The problem of the CNTs-based gas sensor that how to improve the sensitivity, selectivity, response and recovery time need to be solved. In recent years, some studies have shown that carbon nanotubes doped with different atoms or functional groups can make the carbon nanotubes have better adsorption capacity and electronic structure, so it can expand the application range of carbon nanotubes to solve the problem above. Peng etc.[11] have found that the modification on the surface of SWCNTs can change the chemical activity of the SWCNTs wall by ab initio molecular dynamics simulation. If parts of C atoms on the SWCNTs are replaced by B or N atoms, SWCNTs can absorb CO_2 and H_2O molecules. Yeung etc.[12] have studied the electronic properties before and after Pt-doped SWCNTs adsorbed NH_3 and CH_4. The data of density of states of system and molecular orbital are obtained by calculation. After adsorbing gas molecules, the electronic structure of Pt-doped SWCNTs was strongly influenced by the gas molecules, and the gas sensor based on Pt-doped SWCNTs is proposed. In this paper, we perform the experiment that using hydroxyl modified and carboxyl modified SWCNTs to detect H_2S and SO_2, the characteristic gases of partial discharge in GIS, respectively.

Experimental

Materials

The SWCNTs used in the experiment are purchased from Chengdu Institute of Organic, Chinese Academy of Sciences. The SWCNTs are black powder and the parameters of SWCNTs are shown in Tab.1. Potassium hydroxide, ethanol and other reagents used in the experiment are all analytical grade reagents. The water used in the experiment is deionized water.

Tab.1 Parameters of SWCNTs

Purity(wt%)	Length(μm)	Diameter(nm)	Surface Area(m^2/g)
>90%	1-3	1-2	380

Hydroxyl modification of SWCNTs

First, 0.2g SWCNTs are mixed with 4g potassium hydroxide in the ball milling tank, and the appropriate amount of ethanol is added, milling for 15hours. Then the reactants are washed by deionized water to neutral. Finally, SWCNTs are put into the oven under 100℃ for use.

Carboxyl modification of SWCNTs

Carboxyl modified SWCNTs can be obtained by the following steps. First, treat the SWCNTs with the mixture of H_2O_2 and H_2SO_4 (volume ratio 1:3). After that, treat the SWCNTs with the mixture HNO_3 and H_2SO_4 (volume ratio 1:3). Then wash the treated suspension of SWCNTs to neutral with deionized water, and filter the SWCNTs out of the solution with filtration paper whose holes diameter is 0.1μm. At last, put the SWCNTs into the oven under 100℃ for use.

Preparation of SWCNTs based gas sensor

The structure of substrate of SWCNTs based gas sensor is shown in Fig.1. The substrate is made from printed circuit board. The substrate is etched with interdigital copper electrodes. The thickness of the copper is about 30μm, and the width of that is 1mm. The space between the electrodes is 1mm.

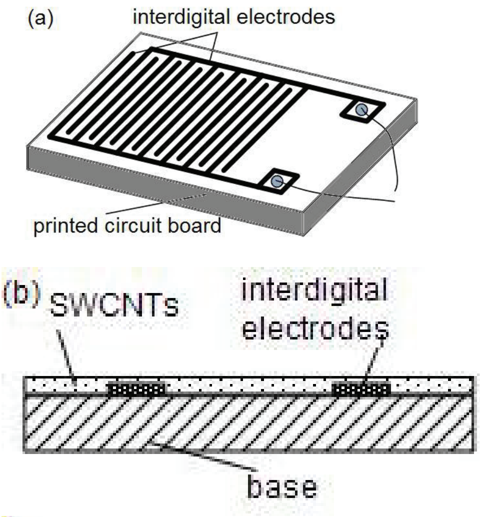

Fig.1. Structures of substrate (a) without SWCNTs; (b)coated with SWCNTs

First, the modified SWCNTs are put into a beaker containing appropriate ethanol solution, after which put the beaker in the ultrasonic device and treat them in it for an hour in order to make the SWCNTs clusters spread out. Then traces of the mixed droplets are dropped onto the surface of the substrate. Finally, the substrates coated with SWCNTs are placed in an oven and bake the substrates at 80℃ for two hours. The process is repeated for several times until uniformly dense SWCNTs film appears on the surface. According to the steps above, we fabricate hydroxyl modified SWCNTs and carboxyl modified SWCNTs based gas sensor, respectively.

The resistance of the SWCNTs gas sensor is measured by impedance recorder in the gas sensing experiment. The H_2S and SO_2 used in the experiment are both standard gases whose concentrations are both 50μL/L. The experiment is performed at 25℃. The response of the gas sensor S is defined as

$$S = \frac{|R - R_0|}{R_0} \times 100\%$$

where R represents the resistance upon exposure to the test gases and R_0 is the initial resistance measure in vacuum, respectively.

Experiment apparatus and procedures

The experiment apparatus mainly include the gas chamber and impedance recorder. The structure of the gas chamber is shown in Fig.2. It mainly includes the cylinder, vacuum gauge, pressure gauge, inlet, outlet switch valve and so on.

The experimental procedures are as follows.

First, turn off the valves of the pressure gauge and inlet, and turn on the valve of the vacuum gauge. Then turn on the vacuum pump.

After a few minutes, turn off the vacuum pump and the valve of outlet, and leave it for 12 hours. Observe the display of the vacuum gauge to check out the air tightness of the cylinder. If the air tightness satisfies, put down the temperature and initial resistance R_0 of the SWCNTs based gas sensor.

Then the standard gas is injected into the cylinder, at the same time recording the resistance R until the resistance does not change any more. At last, the cylinder is drawn into the vacuum.

Following the steps above, the gas response of hydroxyl modified and carboxyl modified SWCNTs to H_2S and SO_2 are measured, respectively.

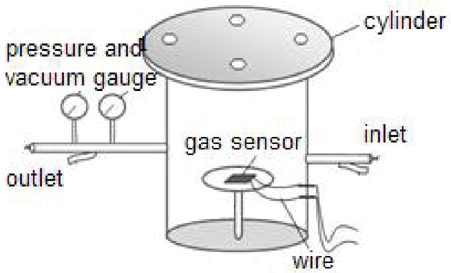

Fig.2. Structures of gas chamber for testing sensors

Results and discussion

Infrared spectrum of the hydroxyl modified and carboxyl modified SWCNTs

The surface chemical compositions of the modified SWCNTs are analyzed by the infrared spectrum in order to understand whether the hydroxyl or carboxyl functional groups are connected on the surface of it after modification. Fig.3 and Fig.4 show the infrared spectrum of the hydroxyl modified and carboxyl modified SWCNTs, respectively. The infrared spectrometer used is Nicolet Magna IR 550II.

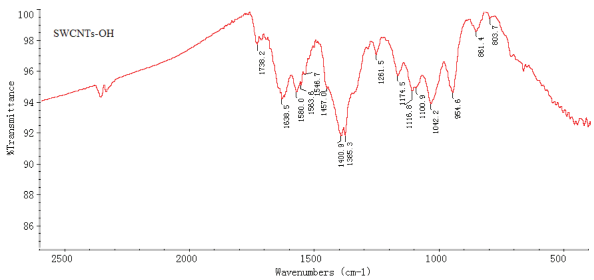

Fig.3. Infrared spectrum of hydroxy modified SWCNTs

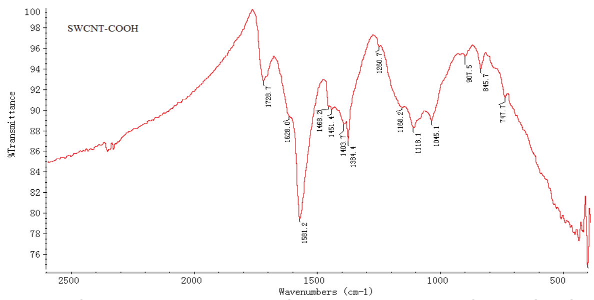

Fig.4. Infrared spectrum of carboxyl modified SWCNTs

In Fig.3 there is a peak at 1400 cm^{-1}, and it is the bending vibration peak of -OH. What's more, there is also a peak at 1100 cm^{-1}, the stretching vibration of –OH. Therefore, we can infer that the hydroxyl is connected on the surface of hydroxyl modified SWCNTs.

As can be seen from Fig.4, a strong characteristic absorption peak appears at 1580cm^{-1}, which is the peak of antisymmetric stretching vibration of COO of carboxylic ion. The absorption peak at 907cm^{-1} is for the outofplane bending vibration of the COH of carboxylic acid. What's more, the peak at 747cm^{-1} is for the variable-angle vibration of COO. Therefore, we can infer that the carboxyl is connected on the surface of SWCNTs modified by carboxyl.

Response of the hydroxyl modified and carboxyl modified SWCNTs to H_2S and SO_2

The gas sensing response curves of hydroxyl modified SWCNTs to H_2S and SO_2 are shown in Fig.5. As can be seen in Fig.5, the sensitivities of hydroxyl modified SWCNTs to H_2S and to SO_2 are 1% and 0.6%, respectively. The sensitivity to H_2S is approximately twice than that to SO_2. Fig.6 shows the gas sensing response curves of carboxyl modified SWCNTs to H_2S and to SO_2. The sensitivities of carboxyl modified SWCNTs to H_2S and SO_2 are 8.4% and 2%, respectively. The sensitivity to H_2S is almost 4.2 times than that to SO_2.

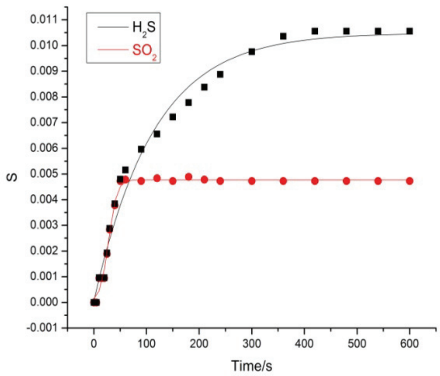

Fig.5. Gas sensing response curve of hydroxyl modified SWCNTs to H_2S and SO_2

Comparing Fig.5 with Fig.6, both the hydroxyl modified SWCNTs and carboxyl modified SWCNTs present better sensitivity to H_2S. What's more, the sensitivity of carboxyl modified SWCNTs to H_2S is greater than that of hydroxyl modified SWCNTs to H_2S. It shows the same results to SO_2.

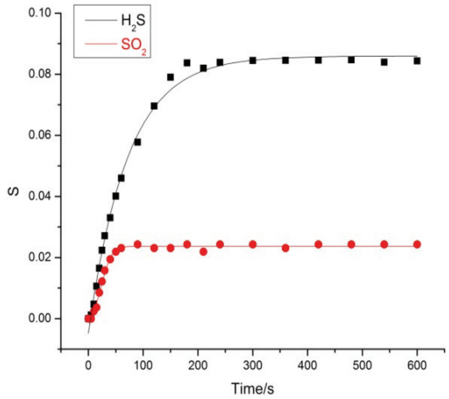

Fig.6. Gas sensing response curve of carboxyl modified SWCNTs to H_2S and SO_2

From the aspect of gas sensor response time, the response time of the two kinds of sensors to SO_2 are approximately both 50s. The response time of hydroxyl modified SWCNTs to H_2S is about 250s, while the response time of carboxyl modified SWCNTs to H_2S is only 120s. Therefore, compared with the hydroxyl modified SWCNTs, the carboxyl modified SWCNTs show faster response to H_2S.

Discussion

The gas sensing response mechanism of the carbon nanotubes is as follows. The Fermi level changes when the carbon nanotubes interact with the gas molecules, leading to the change of the resistance at the macro. When the oxidizing gas molecules interact with the carbon atoms of the carbon nanotubes surface, the electron cloud of the carbon nanotubes surface will tend to the gas molecule, which leads to the charge transferring from the carbon nanotubes to gas molecules. The loss of electrons of the carbon nanotubes increases the concentration of hole carrier, so the conductivity of carbon nanotubes rises. When the reducing gas molecules interact with the carbon nanotubes, the charges transfer from the gas molecules to carbon nanotubes, occupying the holes of the carbon nanotubes. Therefore, the concentration of carrier decreases, which decreases the conductivity of carbon nanotubes.

H_2S and SO_2 are both reducing gases, so the conductivity of carbon nanotbubes will decrease when H_2S or SO_2 interacts with the carbon nanotubes. The reducibility of H_2S molecule is greater than that of SO_2, so the charge transferring amount from H_2S gas molecules to carbon nanotubes is more than that from SO_2 gas molecules to carbon nanotubes. Therefore, either the hydroxyl modified SWCNTs or carboxyl modified SWCNTs shows better gas response to H_2S than to SO_2.

Both –OH on the surface of the hydroxyl modified SWCNTs and –COOH on the surface of the carboxyl modified SWCNTs present oxidizability, and the oxidizability of –COOH is greater than that of –OH[13]. Therefore, when the H_2S or SO_2 molecules interact with the two kinds of modified SWCNTs, the charge transferring amount from gas molecules to the carboxyl modified SWCNTs is greater than that from gas molecules to the hydroxyl modified SWCNTs. Therefore, the carboxyl modified SWCNTs shows better sensitivity than the hydroxyl modified SWCNTs to both H_2S and SO_2. The reason why the carboxyl modified SWCNTs shows faster response time to H_2S than hydroxyl modified SWCNTs is also because the stronger oxidation of carboxyl modified SWCNTs to some extent.

Conclusions

In this paper, intrinsic SWCNTs are modified by hydroxyl and carboxyl, respectively. Two kinds of gas sensors based on the modified SWCNTs are fabricated. The gas sensing response characteristics of the modified SWCNTs to H_2S and SO_2 which are the characteristic gases of internal latent insulation defects are studied by experiment. H_2S and SO_2 used in the experiment are standard gases whose concentrations are both 50μL/L. The results show that the sensitivity of both two modified SWCNTs to H_2S is higher than that to SO_2. The sensitivity of SWCNTs modified by carboxyl to H_2S is higher than that of SWCNTs modified by hydroxyl to H_2S, and the same for SO_2. What's more, the response time of the SWCNTs modified by carboxyl to H_2S is much shorter than that of the SWCNTs modified by hydroxyl to H_2S. In summary, from the aspect of sensitivity and response time, the SWCNTs modified by carboxyl has better gas response characteristics than SWCNTs modified by hydroxyl in detecting H_2S and SO_2.

Acknowledgments

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REFERENCES

[1] Tang Ju. Study of outer sinsors for on-line monitoring partial discharge in GIS and interference suppression with complex wavelet, Chongqing, China: Chongqing University, 2004.
[2] Iijima S. Helical microtubules of graphitic carbon, Nature. 354 (1991), No.6348, 56-58.
[3] White C T, Todorov T N. Carbon nanotubes as long ballistic conductors, Nature, 393 (1998), No. 6682, 240-241.
[4] Liu C, Fan Y Y, Liu M, et al. Hydrogen storage in single -walled carbon nanotubes at room temperature, Science, 286 (1999), No.5442, 1127-1129.
[5] Stail C, Chen M, Gelperin A, et al. Dna-decorated carbon nanotubes for chemically sensing, Nano Letters, 5 (2005), No.9, 1774-1778.

[6] Suehiro J, Zhou G, Hara M. Detection of partial discharge in S F_6 gas using a carbon nanotube-based gas sensor, Sensors and Actuators B, 105 (2005), No.2, 164-169.
[7] Bekyarova E, Davis M, Burch T, et al. Chemically functionalized single-walled carbon nanotubes as ammonia sensors, Journal of Physical Chemistry B, 108 (2004), No.51, 19717-19720.
[8] Zhang Xiao-xing, Liu Wang-ting, Tang Ju. Study on PD Detection in SF_6 using Multi-wall Carbon Nanotube Films Sensor, IEEE Transactions on Dielectrics and Electrical Insulation, 17 (2010), No.3, 838-844.
[9] Zhang B, Fu R W, Zhang M Q, et al. Preparation and characterization of gas-sensitive composites from multi-walled carbon nanotubes/polystyrene, Sensors and Actuators B, No.2, 109 (2005) 323-328.
[10] Qi P, Vermesh O, Grecu M, et al. Toward large arrays of multiplex functionalized carbon nanotube sensors for highly sensitive and selective molecular detection, Nano Letters, 3 (2003), No.3, 347-351.
[11] Shu P, Kyeongjae C. Ab initio study of doped carbon nanotube sensors, Nano Letters, 3 (2003), No.4, 513-517.
[12] Yeung C S, Liu L V, Wang Y A. Adsorption of Small Gas Molecules onto Pt-Doped Single-Walled Carbon Nanotubes, J. Phys. Chem. 112 (2008), No.19, 7401-7411.
[13] Pan H, Feng Y P, Lin J Y. Ab initio study of OH-functionalized single-wall carbon nanotubes, Phys. Rev. B. 70 (2004),No.24, 245421-245425.

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