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Characterization of Multi-Walled Carbon Nanotube Film Sensor and Ethanol Gas-Sensing Properties

Dongzhi Zhang, Kai Wang, Bokai Xia
College of Information and Control Engineering, China University of Petroleum (East China), Qingdao,
266580, China
e-mail: dzzhang@upc.edu.cn

Abstrak

Sensor pada substrat printed circuit board (PCB) dengan antar elektroda digital (IDE) berbasis film nanotube karbon banyak-dinding (MWNTs) telah dipabrikasi dengan menggunakan lapis-demi-lapis rakitan-sendiri, dan sifat listrik dari sensor film MWNTs diselidiki melalui pembentukan model yang melibatkan sejumlah lapisan rakitan-sendiri dan jarak sentuh IDE, dan juga etanol sifat sensor gas dengan berbagai konsentrasi yang dikarakterisasi pada suhu kamar. Melalui pembandingan dengan metode evaporasi termal, hasil eksperimen menunjukkan bahwa sensor film MWNTs lapis-demi-lapis rakitan-sendiri memiliki respon lebih cepat dan perubahan resistensi lebih sensitif bila terkena gas etanol. Sensor yang dikembangan ini, prospektif sebagai sensor untuk deteksi gas etanol dengan kinerja tinggi dan biaya rendah.

Kata kunci: nanotube karbon banyak-dinding, lapis-demi-lapis rakitan-sendiri, sensor gas, karakterisasi listrik

Abstract

Multi-wall carbon nanotubes (MWNTs) film-based sensor on the substrate of printed circuit board (PCB) with inter digital electrodes (IDE) were fabricated using layer-by-layer self-assembly, and the electrical properties of MWNTs film sensor were investigated through establishing models involved with number of self-assembled layers and IDE finger gap, and also its ethanol gas-sensing properties with varying gas concentration are characterized at room temperature. Through comparing with the thermal evaporation method, the experiment results shown that the layer-by-layer self-assembled MWNTs film sensor have a faster response and more sensitive resistance change when exposed to ethanol gas, indicated a prospective application for ethanol gas detection with high performance and low-cost.

Keywords: multi-wall carbon nanotube, layer-by-layer self-assemble, gas sensor, electrical characterization

1. Introduction

Gas detection plays a very important role in the various fields of atmospheric pollution monitoring, toxic gas or volatility poisonous chemical leak, power transformer diagnosis, human health diagnosis [1], [2]. Gas sensors based on nanomaterials are also emerging in a large way as the recent trend indicates the preference towards potential applications. Carbon nanotubes (CNTs) have attracted extensive attention because of their unique physical, chemical and electrical properties since their discovery by Iijima in 1991, nowadays they have been used as one of the ideal materials for gas sensors [3], [4]. Carbon nanotubes-based thin film can convert the information in relation with gas type and concentration into electrical signals when exposed to different gases, such as NO_2, NH_3, CH_4, and humility sensor has also been mentioned [5-11].

Currently, the detection and sensing of ethanol gas is important for a variety of purposes including ethanol production, industrial chemical processing, fuel processing and use, societal applications, and physiological research on alcoholism. A large number of commercial ethanol measurement systems are available for several of these applications, but in general, these systems are operated at relatively high power levels and high-temperature, are expensive and bulky, and possess functionality that is more limited than required for a number of applications. Therefore, the use of CNTs-based devices for detection of ethanol vapor has received some attention for sensing in a smaller-size, inexpensive and portable way. L. Yi Sin et al fabricated the Si-substrate sensors using an AC electrophoretic technique so as to form

bundled CNTs sensing elements, and proved the feasibility of turning the CNTs sensors into a commercialized alcohol sensor with ultra-low power requirements [12]. Brahim et al fabricated ethanol sensors by drop-casting dilute dispersions of a metal-CNT hybrid material onto quartz substrate electrodes at room temperature, and exhibited significantly improved response to ethanol vapor over a wide concentration range compared to the pure CNT sensor [13]. Liang et al fabricated gas sensors from multiwalled carbon nanotubes (MWNTs) coated with a thin tin oxide layer, which shows good response when dispersed in ethanol gas [14]. Lately, Phetchakul et al have studied the environment temperature affect to alcohol detecting and heated CNTs film after alcohol detecting for a good chemical sensor application [15]. SnO_2/MWNTs have been studied as gas sensing materials, and they exhibit improved ethanol sensing properties such as higher sensitivity and quicker response/recovery at 300 °C [16]. However, the above methods mentioned have some weaknesses, for instance, some of them needs high temperature to work, while some fabrication processes are complicated and depend on some special instruments.

An alternative cost-effective approach, a solution-based bottom-up assembly process called layer-by-layer (LbL) self-assembly, allowed for sequential adsorption of nanometer-thick monolayers of oppositely charged polyelectrolytes and carbon nanotubes to form a homogeneous hierarchical membrane with a molecular-level control over the architecture [17-18]. Here we fabricated a MWNTs film-based sensor on the substrate of printed circuit board (PCB) with interdigital electrodes (IDE) using LbL self-assembly, and the electrical properties of MWNTs film sensor involving in IDE finger gap and self-assembled layers are investigated, and also its ethanol gas-sensing properties are characterized. The testing results of the LbL self-assembled MWNTs film sensor indicated a prospective application for ethanol gas detection with high performance and low-cost.

2. Experiment
2.1. Experimental Materials

MWNTs were chemically treated with the concentrated acid (3:1 for 98 wt% H_2SO_4 : 70 wt% HNO_3), and dispersed in deionized (DI) water with concentration of 2 wt.%. The functionalized MWNTs were negatively charged by carboxylic groups, facilitating the uniformly dispersion of MWNTs into DI water.
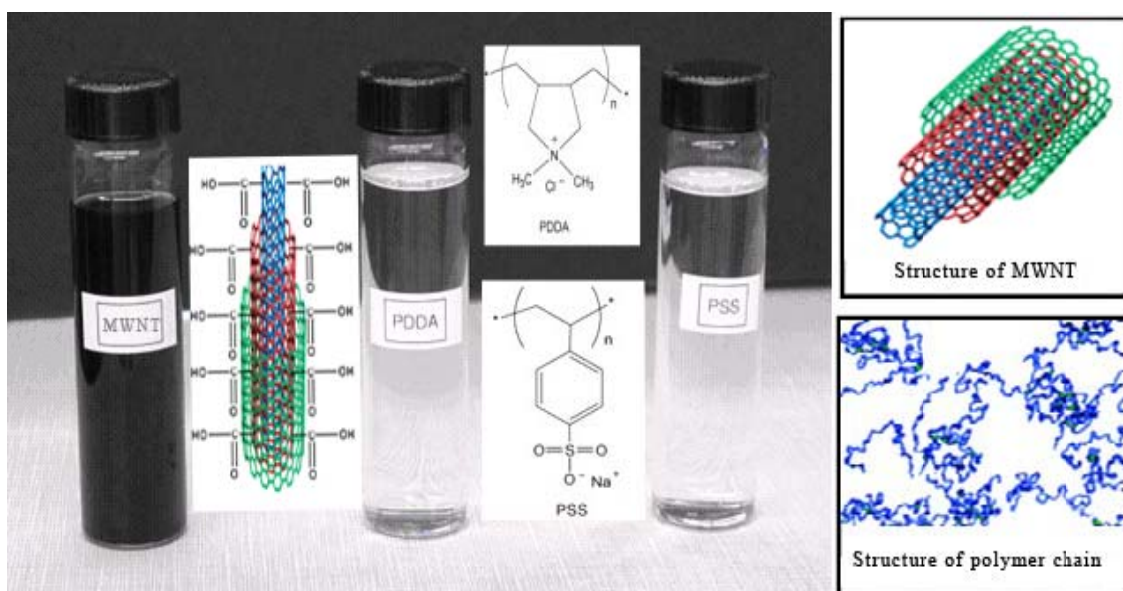

Figure 1. Main experiment materials

Polyelectrolytes used for LbL assembly were 1.5 wt% poly (diallylimethyammonium chloride) [PDDA (Sigma-Aldrich Inc.), molecular weight (MW) of 200K-350K, polycation] and 0.3 wt% poly(sodium 4-styrenesulfonate) [PSS (Sigma-Aldrich Inc.), MW of 70K, polyanion] with 0.5 M NaCl in both for enhancing the ionic strength and polyions adsorption. Photographs, chemical structure and macromolecule chain for functionalized-MWNT, PDDA and PSS are shown as followed in Figure 1.

2.2. Fabrication of Self-Assembled MWNT's Film Sensors

Interdigital electrodes are printed on printed circuit board with an outline dimension of 1×1cm, the IDE finger gap used are 200μm, 300μm, 400μm and 500μm, the electrode material is Ni/Cu. The Sketch of the thin films is shown as Figure 2, sensing material MWNTs and binding materials PDDA and PSS are fabricated on the substrate of PCB-IDE device. Here we used LbL self-assembly method to fabricate MWNT thin films, which is illustrated as Figure 3. First, immerse the preprocessed IDE device into solution PDDA for 10min, then rinse it with DI water and dry with nitrogen flow, followed by immersion in solution PSS for 10min, then rinse and dry. Repeat once again to form two precursor layers of PDDA/PSS on the substrate for charge enhancement. Afterwards, alternately immerse the IDE substrate into solutions PDDA and MWNTs for n cycles, the immersion time here used is 10 min for PDDA and 15 min for MWNTs, and intermediate rinsing with DI water and drying with nitrogen flow are required after each monolayer assembly to reinforce the interconnection between layers. Finally the multilayer films $(PDDA/PSS)_2(PDDA/ MWNTs)_n$ are formed, where n is 1, 3, 5, 7, 9 ,11 here, and heat the self-assembled MWNTs film devices under 80 ºC for 2 hours as the last step.
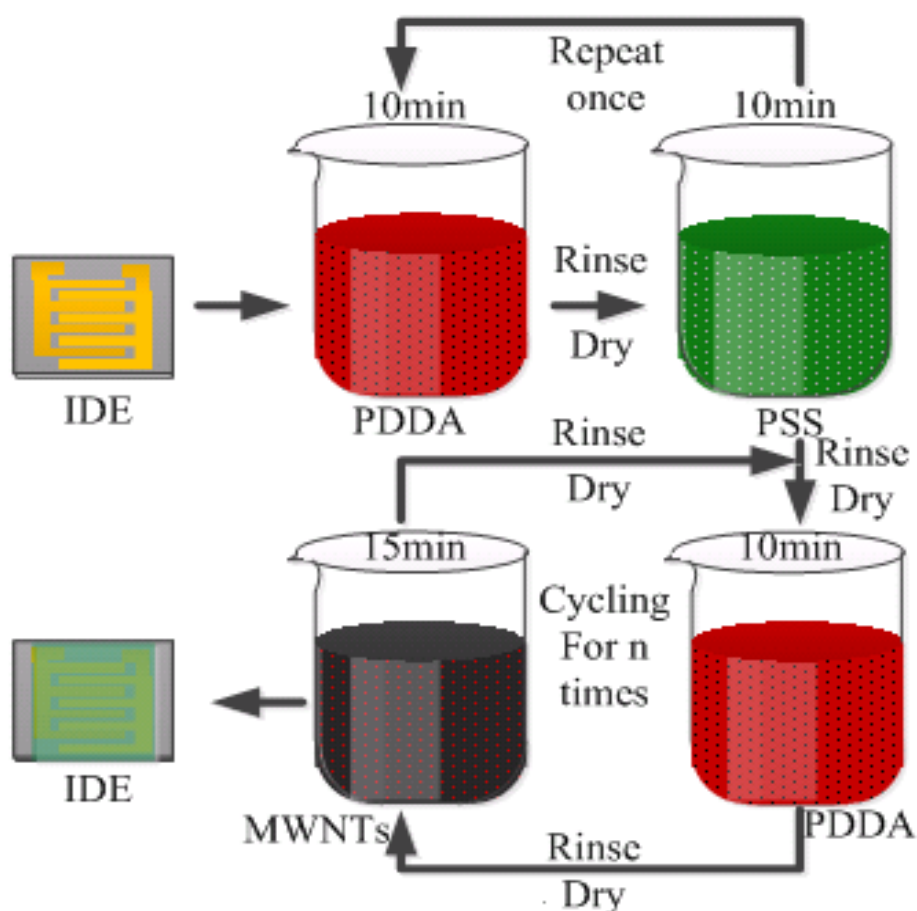

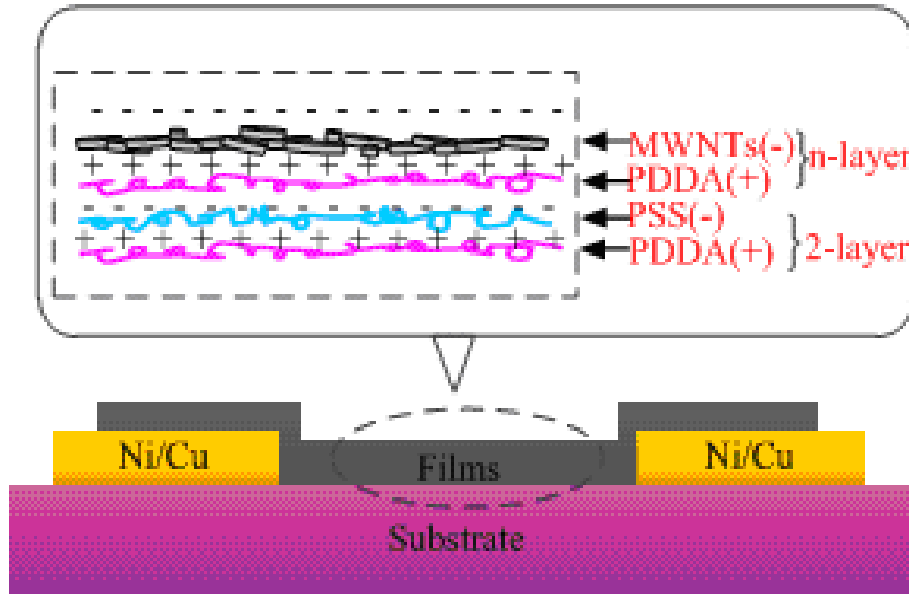Figure 2. Sketch of layer-by-layer self-assembled MWNT film sensors

Figure 3. Outline of layer-by-layer self-assembly process

3. Result and Analysis
3.1. Electrical Characterization of the Self-Assembled MWNT Film Sensors

The electrical properties of the fabricated MWNT film devices with different layer numbers are characterized by the data acquisition unit. Figure 4 plots the relationship of the film resistance versus self-assembled layer number and finger gap, and indicates that the film resistance decreases with the increasing of the assembled layers under the same IDE finger gap, and also shows that decreases with the increasing of the IDE finger gap under the same layer numbers. The curves in Figure 4 are fitted using the model $f(x)=a/x^2+b/x+c$, where a, b, c are the undetermined coefficients, x represents the cycle numbers of self-assembled (PDDA/MWNTs) bi-layers. Table 1 indicates the calculated results for model fitting parameters.
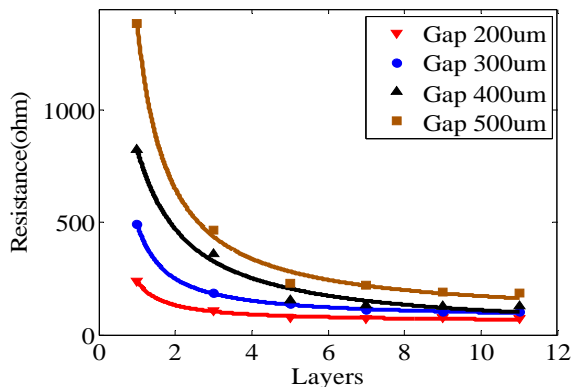

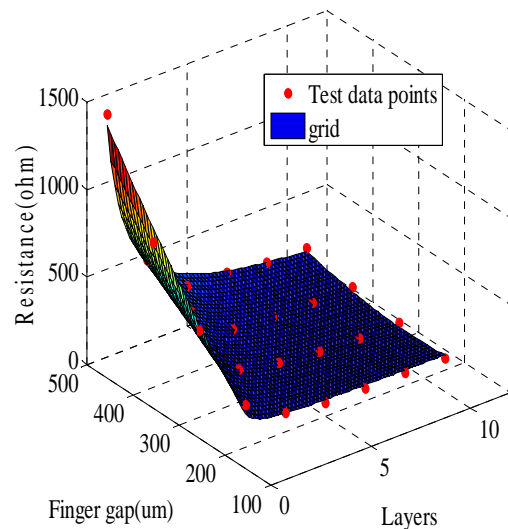Figure 4. Relations between film resistance and self-assembled layers with different finger gaps

Figure 5. Three-dimensional numerical simulation of the film resistance versus film layer numbers and IDE gap

In order to further investigate the cross-influence of both finger gap and self-assembled layers on the film resistance, a three-dimensional numerical model $f(x,y)=a/x^2+b/x+cy+d(y/x)+e$ is employed, where a, b, c, d, e are the undetermined coefficients, x and y are the cycle numbers of self-assembled (PDDA/MWNTs) bi-layers and IDE finger gap respectively. The simulation results are shown in Figure 5, and the calculated results for the model parameters are listed in Table 2. Coefficient of determination R^2 is used here as a measure of how well the models fits the experiment data, which is determined as:

$$R^2 = 1 - \sum_{i=1}^{m}(y_i - \hat{y}_i)^2 \bigg/ \sum_{i=1}^{m}(y_i - \frac{1}{m}\sum_{i=1}^{m}y_i)^2 \qquad (1)$$

where y_i and $\hat{y}_i$ represent experimental measured values and predictive values of model, respectively, and m represents number of measuring points. R^2, listed in the Table 1, shown the selected models for data fitting are appropriate, and so disclosed the relationships of the film resistance versus assembled layer number and IDE finger gap.

Table 1. Results for model fitting with different IDE finger gaps

Finger Gap d (μm)	R^2	undetermined coefficients		
		a	b	C
500	0.9963	316.2	1002	69.53
400	0.9877	-213.5	1031	9.05
300	0.9994	122.1	302.8	69.12
200	0.9963	59.65	121.4	57.16

Table 2. Results for mixture model fitting of three-dimensional numerical simulation

R^2	undetermined coefficients
0.9822	a=71.13, b= -735.8, c= -88.95, d=3858, e=82.35

3.2. Characterization of Ethanol Gas-Sensing Properties

The ethanol gas-sensing experiments are carried out at room temperature, Figure 6 shows the experiment setup for ethanol gas-sensing properties, which, are characterized by using Agilent 34970A. Inject ethanol solution into the sealed beakerflask using a micropipettor and evaporates it completely through heating. Expose the self-assembled MWNTs film sensor (IDE finger gap d=200μm and layer number n=5) into ethanol gas, the adsorption of ethanol gas produced a measurable change in the MWNTs film resistance. The resistance responses to varying ethanol-gas concentration are recorded. Figure 7 shows the ethanol gas sensing response of the MWNTs film sensor in terms of sensitivity change with changing the concentration of ethanol gas. The sensitivity S (percentage change in resistance), is denoted as the ratio $\Delta R/R_{air}$, where ΔR is the difference of resistance of self-assembled MWNTs sensor in the presence of the ethanol gas and in dry air, R_{air} is the resistance of the sensor in dry air. The results in Figure 7 illustrates that the sensitivity of the MWNTs film sensor increases along with the increasing of gas concentration, and reachs beyond 4% when exposing to ethanol gas concentration of 30 kppm.

Anthor alternative method known as thermal evaporation method is used to fabricate MWNTs sensors for making a comparision with LbL self-assembly method. In thermal evaporation method, the same MWNTs solution and PCB-IDE substrate are employed, and the MWNTs solution is driped on the substrate surface and then place it under 80 °C for more than 2 hours for drying and forming a MWNT layer. Figure 8 shows the compressive results in response for the two methods when alternating expose to ethanol gas concentration of 30kppm and dry air for three cycles. From the curves in Figure 8 we find that the sensitivity response of LbL self-assembly method is more than two times bigger than that of thermal evaporation method. The response time of LbL self-assembly method is about 10s and the sensitivity reaches 4.1%, while those of evaporation method is around 15s and 1.98%, and both the

recovery time is about 30s. The LbL self-assembled sensor architecture features advantages such as smaller-size, inexpensive and swift response, and enjoys extensive applications.
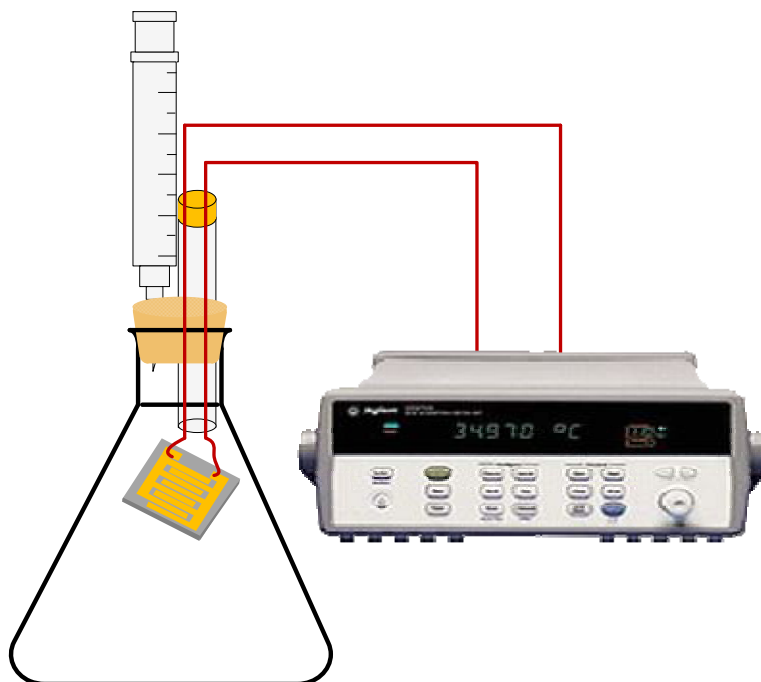

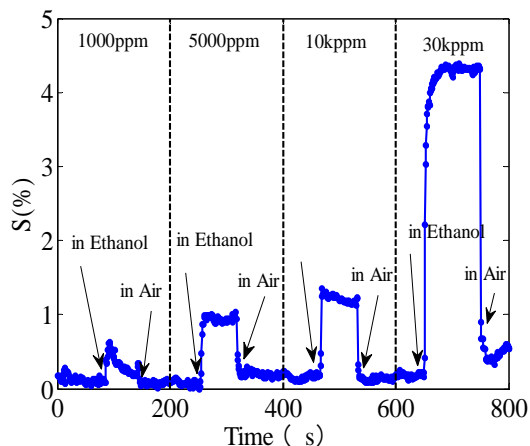Figure 6. Experiment setup for ethanol gas sensing

Figure 7. Sensitivity change for self-assembled MWNTs film sensor with varying ethanol-gas concentration
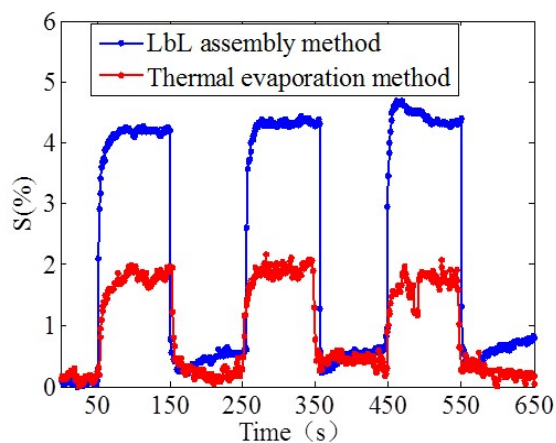

Figure 8. Response to 30 kppm ethanol gas for LbL assembly and thermal evaporation method

It is indicative that the MWNTs film sensor achieves the conversion of the information in relation with ethanol gas concentration into electrical signals. There is an increase of surface potential and subsequent blocking of the movement of conduction electrons when ethanol gas molecules attached on the surface of MWNTs film, where carboxyl functional groups act as adsorption activation center. The gas sensor presents an increase of resistance in the ethanol gas, one probable reason is that dipole-dipole interactions between the -COOH groups on MWNTs and ethanol molecules leading electrons transfer between the surface and the internal,

appearing as resistance increasing. Another reason perhaps is that the adsorption of ethanol molecules directly causes the swelling of the polymer and the increase of tunneling barriers between MWNTs, resulting in an increase of the film resistance.

4. Conclusion

We fabricated MWNT film devices on the substrate of PCB-IDE using LbL self-assembly as gas sensors, the electrical properties of MWNTs film devices were investigated through establishing models involved with number of self-assembled layers and IDE finger gap, and also its ethanol gas-sensing properties are characterized at room temperature. As shown by the experimental results, the LbL self-assembled MWNTs film sensor have a fast response and sensitive resistance change when exposed to ethanol gas, indicated a prospective application for ethanol gas detection with high performance and low-cost.

Acknowledgements

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