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Comparative Study on the Detection Characteristics of C_2H_2 in Various ZnO Nanosensors

To cite this article: Yingqi Qiang 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **490** 022018

Comparative Study on the Detection Characteristics of C_2H_2 in Various ZnO Nanosensors

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Abstract. Acetylene (C_2H_2) is one of the major fault characteristic gases dissolved in the oil of power transformer, which can reflect the discharge fault of transformer effectively. This paper presents three kinds of ZnO nanosensors with different morphology and structure. Based on the laboratory platform, their detection characteristics and gas sensitive mechanism of dissolved C_2H_2 in transformer oil are studied. The results indicate that, owing to the larger specific surface area, the flowerlike ZnO nanosensor maintains good linearity and stability and has higher sensitivity and rapider response than the rod-like and granular ZnO nanosensors. The results provide a new idea for the research of high performance C_2H_2 ZnO sensor.

1. Introduction

Power transformer, a hub device connecting different voltage levels, plays a significant role in the transmission and transformation of power system. Its safe and reliable operation is very important to the security and stability of the whole power system. At present, large power transformers are mainly oil-immersed transformers, and the inner insulation of such transformers is mainly oil-paper insulation. On the long run, the insulating oil, insulating paper and insulating cardboard will age and crack gradually under the action of such electricity and heat, then the cracking will produce various trace characteristic gases which dissolve in the insulating oil of transformer. According to the composition, content and producing regulation of the major characteristic gas, the transformer's insulation status can be determined, and the type, degree and development trend of the transformer's potential fault can be predicted.[1-5] When there is spark and arc discharge in oil of power transformer and arc discharge fault in oil paper insulation, the characteristic gas with C_2H_2 gas as the main component will be produced. Monitoring the gas content of C_2H_2 can predict the internal potential faults of transformers, help to monitor the operation status of transformers in real time and realize the early diagnosis of faults. Commonly used methods for detecting the dissolution of C_2H_2 gas in transformer oil include metal oxide semiconductor sensor, gas chromatography electrochemical sensor method, Fourier transform infrared spectrum, photoacoustic spectrum and Raman spectrum.[6,7] As the core of on-line monitoring device for dissolved gas in oil, gas sensing technology directly affects the accuracy, stability and service life of the monitoring system.

In recent years, gas detection device in transformer oil with metal oxide semiconductor gas sensor has been widely used in on-line monitoring of power transformers. Gas sensor made of ZnO is sensitive to the fault characteristic gases dissolved in oil, such as H_2, CO, CH_4, C_2H_6, C_2H_4 and C_2H_2.[8-10] It is one of the most important sensors used in experimental research and commercial applications to detect gas in oil. However, limitations still exist. For example, the content of C_2H_2 dissolved in oil is very low (less than or equal to 5 μL / L). The ZnO gas sensor has disadvantages such as high operating temperature, severe cross sensitivity, poor selectivity and poor stability for long time use.[11] Therefore, it is of great theoretical and practical significance to develop the ZnO gas sensor with excellent performance and apply it to the on-line monitoring device to improve the fault diagnose ability for the sake of the stable operation of transformer's insulation.

In this work, three kinds of hierarchical ZnO nanomaterials with different morphology were prepared by the hydrothermal method using hexadecyl trimethyl ammonium bromide (CTAB) as surfactant. X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) were utilized to microscopically characterize three kinds of ZnO nanostructure. The powder of ZnO was prepared into a sensor by screen printing technology. The gas sensitivity was tested based on the CGS-1 TP intelligent gas sensitivity analysis system, then the reaction mechanism was also analyzed. The results show that the flowerlike ZnO nanosensor has better sensitivity, response recovery and stability to the dissolved trace C_2H_2 gas in transformer oil than the rod-like and granular ZnO nanosensor due to the larger specific surface area. This study provides a new and feasible method for detection of C_2H_2 gas in transformer oil by high performance ZnO sensor.

2. Experimental

Three kinds of ZnO nanopowder with different morphology are prepared by hydrothermal method. [12-14] First, 2.98 g and 0.25 g $Zn(NO_3)_2 \cdot 6H_2O$ were added to 100 mL deionized water, respectively. The ammonia was then gradually dripped and made the pH value of solution become 7. The white suspension was collected and separated furthermore by centrifugation, then cleaned repeatedly with deionized water. Second, 1.83 g and 0.83 g CTAB was added into 50 mL deionized water respectively and mixed with the above white precipitation into a Teflon-lined stainless steel autoclave with 100 ml capacity and was heated to 150 °C for 20 h. After cooled to room temperature naturally, the solution is repeatedly centrifuged for several times with deionized water and anhydrous ethanol. Finally, it is dried to get the flower like and rodlike zinc oxide nanopowder at 60 °C. On the other hand, 3.34 g $Zn(NO_3)_2 \cdot 6H_2O$ was added into 40 mL deionized water, and ammonia was dripped to keep the pH value at 7 and it is stirred continuously at room temperature for 1 h. The white suspension was collected and separated by centrifugation, then washed several times with deionized water. The white precipitation and 0.51 g sodium citrate was added into 50 mL deionized water and transferred into a Teflon-lined stainless steel autoclave with 100 ml capacity and was heated to 200 °C for 10 h. After cooled to room temperature naturally, the solution is repeatedly centrifuged with deionized water. Finally, it is dried to get the granular zinc oxide nanopowder at 60 °C.

XRD was carried out for crystal structure characterization of the prepared ZnO nanopowder. FESEM was used to characterize the surface morphology of the prepared powder.

3. Results and discussion

3.1 The XRD characterization

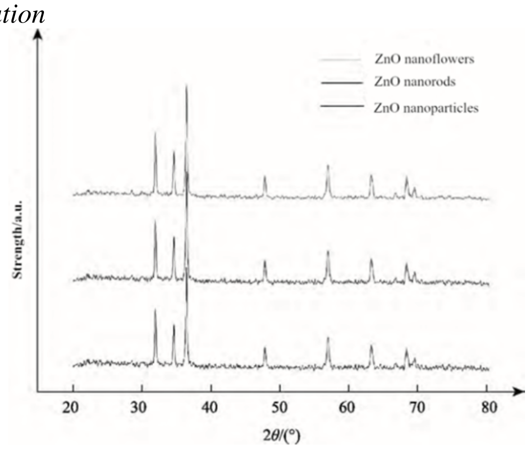

Figure 1. XRD spectra of the ZnO nanopowder with different morphologies.

Figure 1 shows the XRD characteristic results of different kinds of ZnO nanopowder. These diffraction peaks of each sample are consistent with the standard map of ZnO in wurtzite (JCPDS card No. 36-1451), with smooth spectral line and sharp peaks from no other impurities. The results indicate that the prepared samples possess complete grain development, good crystallinity and high purity.

3.2 Morphology characterization

The morphology of three different kinds of ZnO nanopowder can be found in Figure 2. Figure 2(a) shows the surface morphology of ZnO nanoparticles with uniform size and diameter of 300-500 nm. As shown in Figure 2(b), it can be seen that the nanorod with a pointed end has a radius of 40-80 nm and a length of about 3 μm. Figure 2(c) shows the surface morphology of ZnO nanoflower. The nanoflower is composed of multiple nanorods formed by central radiating self-assembly, with a diameter of about 5 μm. All powder grains are uniformly dispersed, which is beneficial to fully contact with gas and promote gas-sensitive reaction.

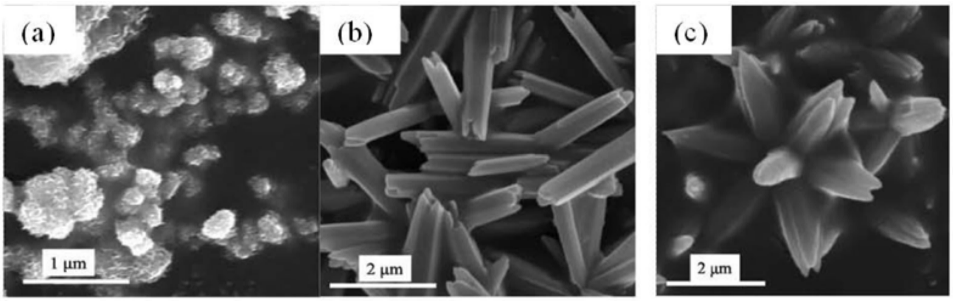

Figure 2. FESEM images of ZnO samples with (a) granular, (b) rod-like, and (c) flower-like morphologies.

3.3 Detection of C_2H_2 gas

Granular, rodlike and flowerlike ZnO plane sensor are prepared by screen printing technology, as shown in Figure 3. Planar gas sensor is mainly composed of gas sensing layer, electrode layer and ceramic insulation layer. The interdigitated silver-palladium signal electrode was prepared on Al_2O_3 ceramic substrate by screen printing technology. The ZnO powder, anhydrous ethanol and deionized water (ratio: 8:1:1) are evenly mixed, and the paste was prepared and evenly applied to the planar substrate electrode. It was put in oven at 60 °C and drying for 4 h. After cooling, the planar gas sensor was produced. The prepared gas sensor ages 2 d under 120 °C in order to improve the stability.

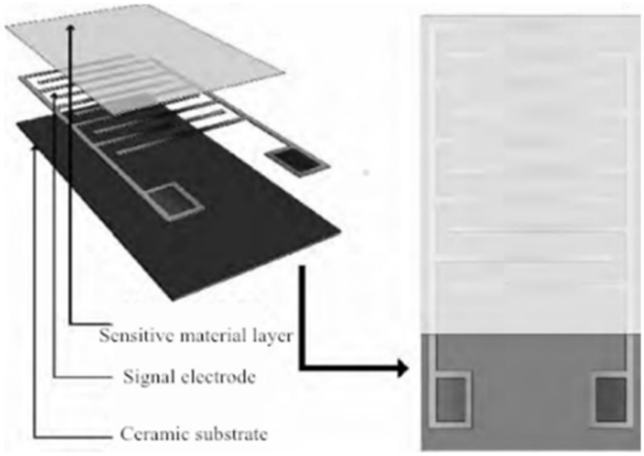

Figure 3. Structure diagram of ZnO gas sensor**.**

For studying how the morphology and structure of the sensitive materials affect the sensing properties, the C_2H_2 gas sensitivity detection was carried out in this paper, such as experiments of working temperature, concentration response, response recovery time, and stability. All tests are conducted at room temperature of 26 °C with the humidity of 35 %.

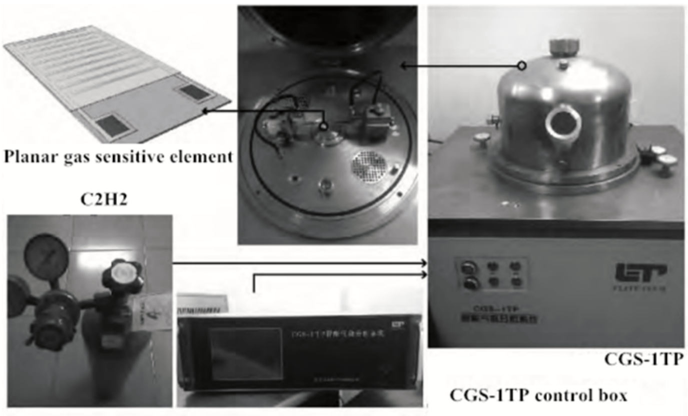

Figure 4. C_2H_2 gas detection platform.

The gas detection platform was built in the laboratory, as shown in Figure 4. The three gas sensors are placed successively in the CGS-1TP analysis system. The instrument can directly measure the resistance R_a of the gas sensor in the air and the resistance R_g in the gas under test, so as to obtain its sensitivity: $S = R_a/R_g$.

Test steps are as follows:

Step 1: place the planar gas sensor in the center of the temperature control platform, adjust the probe position and seal the gas chamber. Set the working temperature to start heating and collect data. When the resistance is stable, record the R_a of the gas sensor in the air.

Step 2: open the vacuum valve and vacuum pump. When air chamber pressure is 1.0×10^3 Pa, close the vacuum valve and the vacuum pump. Open the air distribution valve and inject C_2H_2. When the air chamber pressure reaches 1.0×10^5 Pa, the air distribution system is closed.

Step 3: observe the change of the resistance curve until the resistance value is stabilized again. Record the data R_g and calculate the sensitivity.

Step 4: repeat the above steps, compare and analyze the gas sensing properties of the three nanosensors.

3.4 Gas sensing characteristics of sensor to C_2H_2

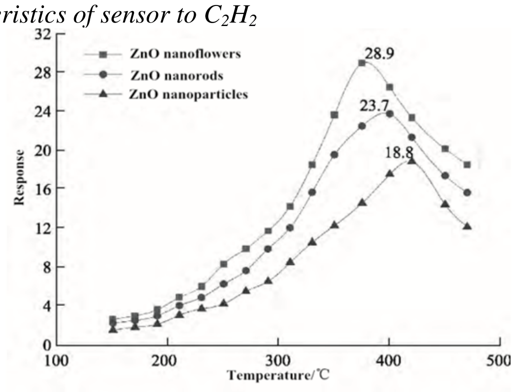

Figure 5. Response of gas sensors to 20 μL/L C_2H_2 at different operating temperatures.

The gas sensor is usually not sensitive to the detected gas at room temperature, so it is necessary for the sensor to work at a suitable temperature to get a high gas sensitivity. The gas sensitive element has an optimum operating temperature for each detected gas, at which the gas sensitive response is maximum. Adjust the temperature from 200 ~ 450 °C, and test sensor response to 20 μL /L C_2H_2. As shown in Figure 5, the response of different sensors rises to the maximum first and then drops along with the increase of operating temperature. The optimum operating temperature of granular, rod-like, and flowerlike morphology of gas sensor for C_2H_2 is 420 °C, 400 °C, and 375 °C, respectively. The corresponding sensitivity is 18.8, 23.7, and 28.9, respectively. The flowerlike gas sensor's optimum operating temperature is lower than rod-like and granular sensors', and its highest response is 1.23 and 1.53 times of theirs, respectively.

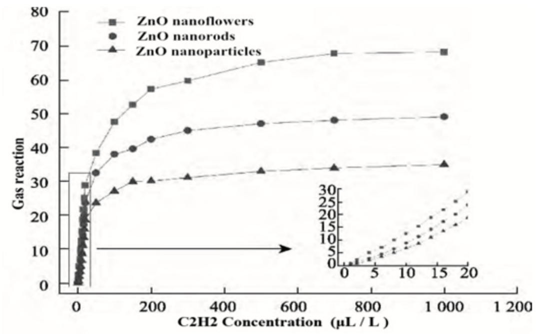

Figure 6. Concentration response curves of ZnO sensors to C_2H_2

At the optimum operating temperatures, the sensitivity of the granular, rod-like and flowerlike ZnO nano gas sensor to 1 ~ 1000 μL/L C_2H_2 gas is measured, as shown in Figure 6. At different concentrations, the flowerlike ZnO gas sensor has higher sensitivity and the fastest growth rate. All three kinds of gas sensors maintain good linearity within the range of C_2H_2 concentration from 1 to 40μL / L. Along with the increase of C_2H_2 concentration, the response of the gas sensor is slowed down and finally reaches saturation.

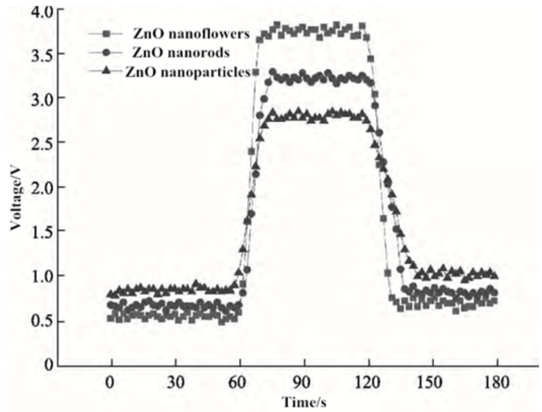

Figure 7. Response and recovery curves of gas sensors to 20 μL / L C_2H_2

Figure 7 shows the response recovery time characteristics of three gas sensors. As can be seen from the Figure 7, the three gas sensitive elements have good response recovery characteristics to C_2H_2. The response degree of the sensor is increasing to the maximum value after injecting 20 μL / L C_2H_2 gas. When the gas recovery system starts up, the sensitivity of the sensor decreases gradually and finally stabilizes to the initial value. The response time is defined as 90 % of the time period that the response needs in order to reach to a stable value since the gas sensitive element begins to contact with the detected gas of which the concentration has a step change. The recovery time is 90 % of the time period for the resistance of the gas sensitive element to return to its normal value in the air beginning with the desorption of the detected gas. In Figure 7, the response-recovery time of granular, rod-like and flowerlike ZnO is 12 ~ 18 s, 10 ~ 15 s and 6 ~ 11 s respectively. All of the three ZnO gas sensors can meet the basic requirements for gas sensitivity detection of dissolved gas C_2H_2 in transformer oil, in which the response time and recovery time of flowerlike ZnO are the shortest, and meanwhile can maintain good repeatability.

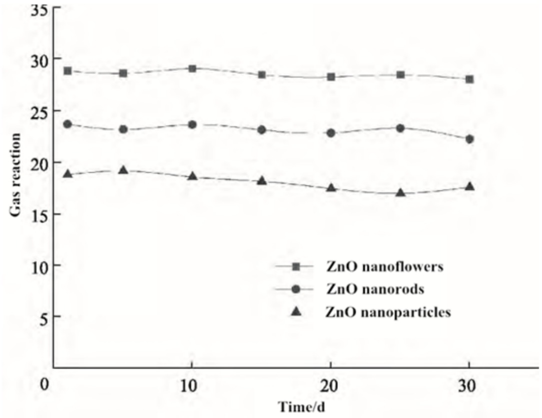

Figure 8. Repeatability and stability test of ZnO gas sensor for 20 L / L C_2H_2**.**

The stability of three ZnO gas sensors was tested, as shown in Figure 8. In one month's cycle, at the optimum temperature of each sensor, the gas sensitivity of 20 μL / L C_2H_2 gas remains basically unchanged, which indicates that the prepared ZnO nanosensor has good stability.

3.5 Analysis on the gas sensitivity mechanism of ZnO nanosensor

ZnO is a typical N-type semiconductor material whose gas sensitivity is under the control of the surface resistance variation. The better gas sensitivity of ZnO nanoflowers can be explained by the surface charge model.[15] The resistance of the gas sensitive element changes when it is placed in different gas environments. We can detect the concentration of the gas according to the change. When ZnO gas sensor is exposed to the air and operating temperature is 100 ~ 200 °C, the oxygen molecules in the air adsorbed on the surface of the sensor. When temperatures rises to 250 ~ 350 °C, the adsorbed oxygen strips the electrons from ZnO conduction band, and dissociates to oxygen ion with one negative charge and bivalent negative charge. When heated up to 300 °C, the O_2 is dominant on the surface of ZnO sensor, making R_a value bigger. Then in C_2H_2 environment, the surface oxygen ion and C_2H_2 will undergo oxidation-reduction reaction, and the captured electron will be released to the conduction band of ZnO, reducing the grain boundary potential barrier and improving the conductivity, so as to reduce the resistance of ZnO gas sensitive element. When the temperature is higher than the optimum operating temperature, the desorption rate of oxygen on the surface surpasses its adsorption rate, resulting in a decrease in sensitivity. The reaction process can be explained by the following equations [16,17]:

$O_2\,(gas) \rightarrow O_2\,(ads)$
$O_2\,(ads) + e^- \rightarrow O_2^-\,(ads)$ ($T < 100°C$)
$O_2^-\,(ads) + e^- \rightarrow 2O^-\,(ads)$ ($100°C < T < 300°C$)
$O^-(ads) + e^- \rightarrow O^{2-}\,(ads)$ ($300°C < T$)
$C_2H_2\,(gas) \rightarrow C_2H_2\,(ads)$
$2C_2H_2\,(ads) + 5O_2^- \rightarrow 4CO_2\,(gas) + 2H_2O\,(gas) + 5e^-$
$C_2H_2\,(ads) + 5O^- \rightarrow 2CO_2\,(gas) + H_2O\,(gas) + 5e^-$

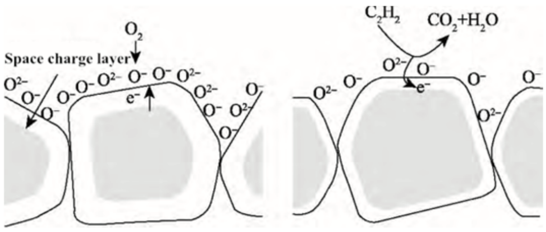

Figure 9. Schematic diagram of the gas sensing reaction process.

The improvement of gas sensitivity of hierarchical and porous ZnO nanoflowers is attributed to the fact that the hierarchical structure has many diffusion channels, so that ZnO can absorb more oxygen in the air and make more adsorbed oxygen on the surface.

The specific surface area of the three ZnO sensor materials are calculated and listed in table 1. The flowerlike ZnO material can provide more diffusion channels and adsorption positions for the gas sensitive reaction, so that it can absorb more oxygen in the air to have more adsorbed oxygen on its surface, facilitating electron transfer. As shown in Figures 5-7, the flowerlike ZnO nanosensor has higher sensitivity, lower optimal operating temperature and better response recovery property than the rod-like and granular ZnO nanosensor. For the prepared nanoparticles, although its size is not large, these particles are united by Van der Waals force, which makes the mesoporous inside the material very small and even blocked, which is not conducive to gas diffusion. The hierarchical flowerlike structure has regular and uniform pores and gaps, allowing the gas molecules to spread more smoothly, and providing more reaction sites and lower packing density. When the sensor is placed in acetylene gas, the conductive state of the element changes rapidly. Therefore, the improvement of C_2H_2 sensing properties of ZnO gas sensor can be realized by effective control of ZnO crystal structure and morphology.

Table 1. Specific surface area and pore structure parameters of ZnO samples.

ZnO sample	Sbet/($m^2 \cdot g^{-1}$)	dp/ nm
Flowerlike	28.6	18.2
Rod-like	25.2	12.5
Granular	18.7	8.4

4. Conclusion

In this paper, three types of ZnO nanosensors with different morphology i.e. the granular, rod-like and flowerlike were successfully prepared and their gas sensitivity to the dissolved C_2H_2 gas in transformer oil was tested. Compared with the granular and rod-like ZnO nanosensors, the flowerlike ZnO nanosensor has higher sensitivity, rapider response, better linearity and stability, and the lowest optimum operating temperature. These advantages depend on the larger specific surface area, more reaction contact points and lower packing density of the flowerlike ZnO nanosensor. The results provide a new idea for on-line monitoring of dissolved C_2H_2 gas in transformer oil by ZnO gas sensor.

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