Gas Sensing Properties of Zn-Doped Anisometric Fe_2O_3 Nanoparticles

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ABSTRACT

In this study, we synthesized nanocrystalline Zn-doped γ-Fe_2O_3 by flame spray pyrolysis under different conditions, and then investigated the gas sensing characteristics of these particles. Transmission electron microscopy (TEM) was employed to characterize the particles. Gas sensors were fabricated by applying the as-synthesized particles on interdigitated electrodes. The response of the gas sensor to acetone vapor in dry synthetic air was measured before and after 3 days of aging. High-temperature flame (H_2/O_2 diffusion) generated nanometer-sized particles; lower temperature flame (H_2/Air diffusion) generated micrometer-sized particles. The Zn-doped Fe_2O_3 nanoparticles showed a gas sensing sensitivity that was 20 times the literature value.[1]The 3–day aging did not cause deterioration in gas sensing ability of the Zn-doped Fe_2O_3 nanoparticles. However, the microparticles lost their gas sensing ability after aging. The results showed that the flame synthesized γ-Fe_2O_3 particles had high gas sensing signal, and were more resistant toward aging than the microparticles.

Keywords: flame spray pyrolysis, gas sensing, sensitivity, aging

1 INTRODUCTION

Gamma-Fe_2O_3 is an n-type semiconductor and has been investigated as a sensor material to detect combustible and toxic gases. In general, pure γ-Fe_2O_3 is not useful in gas sensing applications. Instead, doped Fe_2O_3 has been used in gas sensore. For example, Tao et al.[2] reported that gas sensitivity of γ-Fe_2O_3 to alcohol was greatly improved by doping Y_2O_3 through sol-gel process. Jing [1] found enhanced sensitivity and selectivity of γ-Fe_2O_3 towards acetone, ethanol, methane, and hydrogen by doping it with zinc. Sensors utilizing γ-Fe_2O_3 have many advantages such as high sensitivity, small size, low cost, and ease of fabrication [3-6]. However, the performance stability of γ-Fe_2O_3 based gas sensors has not been systematically investigated. Such knowledge is very useful for development of future materials and better testing techniques to produce sensitive and selective gas sensing materials. In this study, γ-Fe_2O_3 particles doped with 15 mol% zinc were synthesized by flame spray pyrolysis with controlled particle size. The effects of synthesis condition and aging on the sensitivity and the stability of gas sensors made of these particles were determined.

2 THEORY

Gamma-Fe_2O_3 based gas sensor detects gases via variations in their resistances. Oxygen electron vacancies operate as donors and transfer oxygen gas to the negative charged oxygen adsorbates, which play important role in detecting inflammable gases such as acetone, H_2 and CO. Oxygen adsorbates, such as O^-, is known to cover the suface of semiconductive metal oxides in air and eventually the variation in surface coverage of O^- dominates the sensor resistance.[7]

The rate of target gas absorption is influenced by reactions between the sensing material surface and the target gas. These reactions are in turn, affected by catalysts on the material surface, ambient conditions, and sensor temperature. When thermal energy is supplied to γ-Fe_2O_3 nanoparticles, the free charge carriers (electrons for γ-Fe_2O_3) increase and cause a decrease in resistance. Then synthetic air is supplied, the free charge carriers are absorbed by O_2 gas. So the surface of γ-Fe_2O_3 acts as an electric potential barrier which decreases conduction between particles. Reduction gas or other combustible gases remove O_2 gas adsorbed on the γ-Fe_2O_3 surface. This causes the free charge carriers captured in O_2 gas to move into γ-Fe_2O_3 nanoparticles; which weakens the electric potential barrier and increases particle conduction. As a result, the rates of adsorption and desorption influence the sensor's sensitivity to various gasses.

3. METHODOLOGY

3.1 Flame spray pyrolysis apparatus

Zn-doped γ-Fe_2O_3 sensor materials were prepared by flame spray pyrolysis method using H_2 diffusion flame with O_2 or air support. Schematic illustration of apparatus can be found elsewhere.[8] The precursor solution was injected at a steady flow rate into the atomizer vessel using a syringe pump (Cole Parmer, Vernon Hills, IL). Droplets of the atomized solution were carried by the H_2 fuel gas into the flame. Complex chemical reactions and physical changes took place in the flame, and the metal oxide particles were formed. The particles were then collected on an alumina filter. The flame spray pyrolysis method had been described in detail elsewhere.[8].

The precursor solution was prepared by dissolving $Zn(NO_3)_2 \cdot 6H_2O$ (Zinc(III) nitrate hexahydrate, 99.9%, Alfa Aesar) and $Fe(NO_3)_3 \cdot 9H_2O$ (Iron(III) nitrate nonahydrate, 99.9%, Alfa Aesar) in deionized water. The molar concentration of the solution was 0.75 M(mol/L) in terms of total metal ions, with a Zn/Fe atomic ratio of 15/85.

3.2 Gas sensing apparatus

The Zn-doped γ-Fe_2O_3 particles were dispersed in deionized (DI) water under ultrasound sonication. The DI water suspension of the Zn-doped γ-Fe_2O_3 particles was applied drop-wise on an alumina substrate with pre-deposited interdigitated electrodes, on-board heater and built in temperature sensor (Case Western Reserve University, Cleveland, OH). The alumina substrate was heated at approximately 150°C on an electric hot plate to facilitate the evaporation of water. After the evaporation of the water, a coating of Zn-doped γ-Fe_2O_3 particles was formed over the interdigitated electrodes. A gas sensor was thus constructed. For gas sensing testing, the sensor was place in a gas chamber. The gas chamber consisted of inlet, outlet, holder for gas sensor and seven signal/power connectors linked to the sensor. Figure 2 shows how the gas chamber, picoammeter, power supply, bubbler, and mass flow controller were physically connected throughout the experiments.

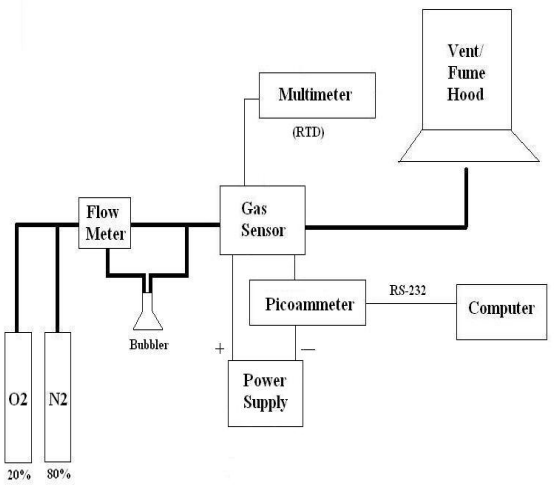

Figure 1 illustrative representation of the connections made throughout the experiments

3.3 Sensor signal measurement

Target and background gas flow is controlled by the mass flow controller and their ratio is calculated using partial pressures. Acetone gas is generated by passing oxygen gas through liquid acetone in the bubbler. Synthetic air was used as the background gas to minimize effects due to humidity in the gasses. Figure 3 shows how the connections were created and the quantities measured.

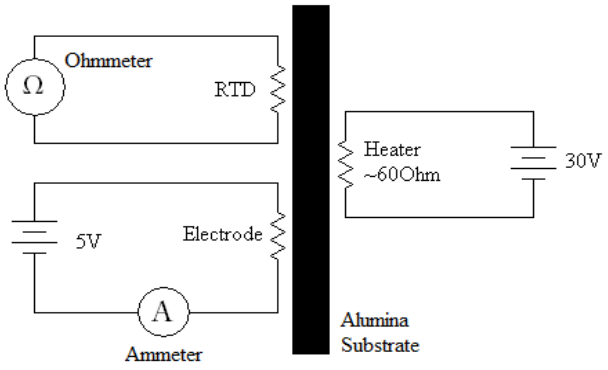

Figure 3 illustrative representation of the electrical circuitry on the electrode

Resistance of the RTD was measured using the ohmmeter setting on a multimeter. During the gas sensing experiment, the resistance of the RTD was monitored with a multimeter (Omega Engineering HHM28) to ensure that the gas sensor temperature was constant within ± 5.5 ˚C. The picoammeter was connected in series with the sensing material to measure the current across the material. A voltage of 5.02 volts was applied across the sensing material to effectively turn the sensing material into a resistor. Equations (1) and (2) show how the current from the picoammeter is converted into the sensor signal. The sensor signal is defined as the ratio of the sensing material's electrical resistance in the background gas, R_b, to the sensing material's electrical resistance in the present of target gas, R_t.

$$S_{signal} = \frac{R_b}{R_t} \tag{1}$$

$$R_{Material} = \frac{V_{Electrode}}{I_{Picoammeter}} = \frac{5.02V}{I_{Picoammeter}} \tag{2}$$

The sensing material's electrical resistance was calculated from the voltage applied on sensor and the current measured with the picoammeter. The picoammeter read/recorded the current once every 2 seconds.

To make aging condition, the gas sensor was placed in the gas chamber for 3 days while maintaining the gas sensor's heater on and existence of ambient air.

4. RESULTS AND DISCUSSION

Figure 4 shows representative TEM images of Zn-doped γ-Fe_2O_3. Particle sizes of Zn-doped Fe_2O_3 formed in H_2/O_2 diffusion flame are much smaller than ones formed in H_2/Air diffusion flame.

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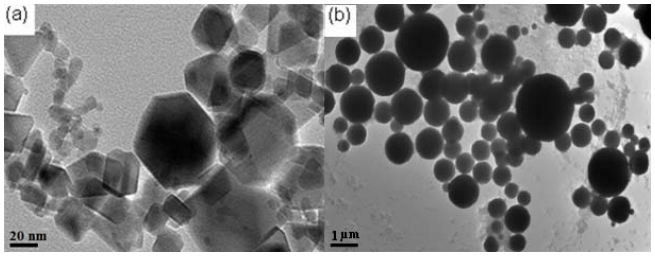

Figure 4 represents TEM images of Zn-doped γ-Fe_2O_3 (a) in H_2:1, O_2:6 flame and (b) in H_2:1, Air:6 flame.

Figure 5 and 6 show how the material responded to various concentrations of acetone gas at those two temperatures. The material made in the hotter flame (H_2:1, O_2:6) provided higher signals at all temperatures than the material made in the cooler flame (H_2:1, Air:6). Surface area affects the amount of gas that comes in contact with the gas sensing material. Smaller particles allow for greater surface area and thus an increased sensitivity to target gas.

Aging effect on the signal of the gas sensor made of different flames was shown in Figure 7 and 8. The gas sensor made of H_2:1, O_2:6 flame showed higher signal after aging, but the gas sensor made of H_2:1, Air:6 flame showed lower signal after aging. It means that the 3–day aging did not cause deterioration in gas sensing ability of the Zn-doped Fe_2O_3 nanoparticles. However, the microparticles lost their gas sensing ability after aging.

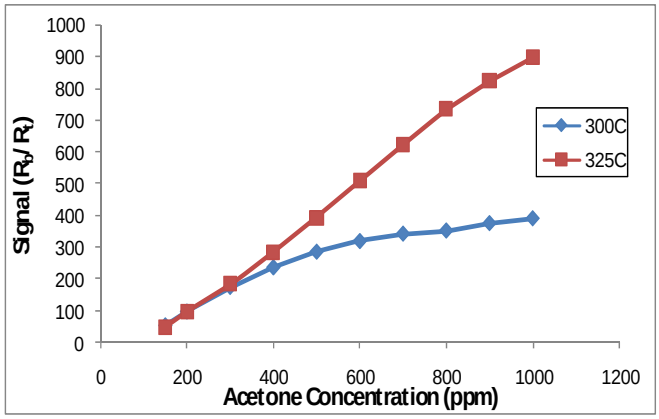

Figure 2 Signal of a sensor made of Zn-doped γ-Fe_2O_3 nanoparticles from a H_2/O_2 flame as a function of acetone concentration; Target temperatures are 300°C and 325°C respectively.

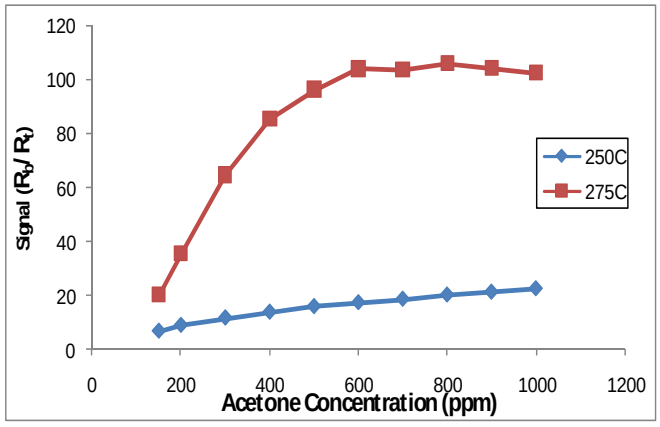

Figure 3 Signal of a sensor made of Zn-doped γ-Fe2O3 nanoparticles from a H_2/Air flame as a function of acetone concentration; Target temperatures are 250°C and 275°C respectively.

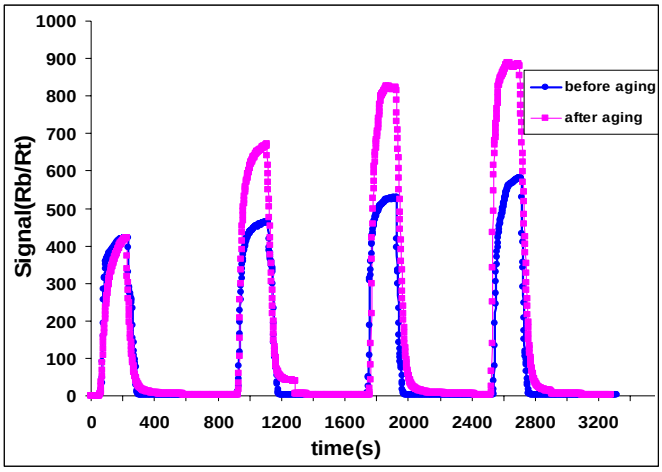

Figure 7 Signal of the sensor material formed in H_2/O_2 flame exposed to different concentrations of acetone; Target temperature is 325°C

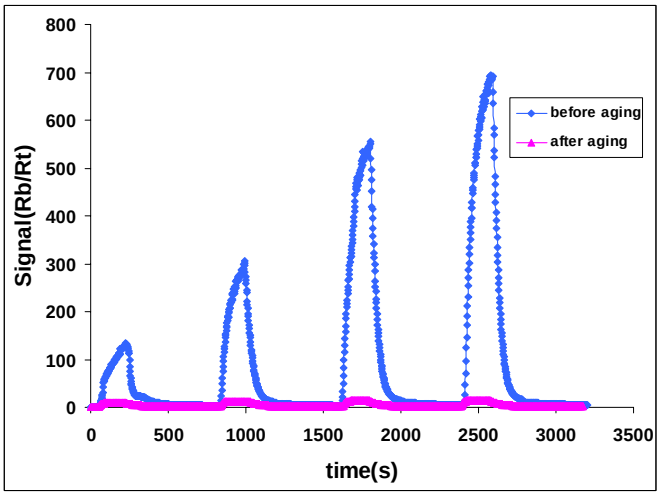

Figure 8 Signal of the sensor material formed in H_2/Air flame exposed to different concentrations of acetone; Target temperature is 275°C

5. CONCLUSION

Fe_2O_3 nanoparticles are formed in H_2/O_2 flames, while microparticle are formed in H_2/air flames. Gas sensors made from nanoparticles appear to be more resistant toward aging than those made from microparticles.

References

[1] Z. H. Jing, Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing 441 (2006) 176-180.
[2] S. W. Tao, X. Q. Liu, X. F. Chu, Y. S. Shen, Sensors and Actuators B-Chemical 61 (1999) 33-38.
[3] M. P. Morales, M. Andres-Verges, S. Veintemillas-Verdaguer, M. I. Montero, C. J. Serna, Journal of Magnetism and Magnetic Materials 203 (1999) 146-148.
[4] B. R. V. Narasimhan, S. Prabhakar, P. Manohar, F. D. Gnanam, Materials Letters 52 (2002) 295-300.
[5] X. S. Niu, W. M. Du, W. P. Du, Sensors and Actuators B-Chemical 99 (2004) 399-404.
[6] J. H. Wang, M. S. Tong, X. Q. Wang, Y. Ma, D. L. Liu, J. K. Wu, D. S. Gao, G. T. Du, Sensors and Actuators B-Chemical 84 (2002) 95-97.
[7] Y. Shimizu, M. Egashira, Mrs Bulletin 24 (1999) 18-24.
[8] B. Guo, Z. P. Luo, Journal of the American Ceramic Society 91 (2008) 1653-1658.