Gas Sensing Properties of Zn-Doped Anisometric Fe$_2$O$_3$ Nanoparticles

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ABSTRACT

In this study, we synthesized nanocrystalline Zn-doped γ-Fe$_2$O$_3$ 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$_2$O$_3$ nanoparticles showed a gas sensing sensitivity that was 20 times the literature value. The 3-day aging did not cause deterioration in gas sensing ability of the Zn-doped Fe$_2$O$_3$ nanoparticles. However, the microparticles lost their gas sensing ability after aging. The results showed that the flame synthesized γ-Fe$_2$O$_3$ 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$_2$O$_3$ is an n-type semiconductor and has been investigated as a sensor material to detect combustible and toxic gases. In general, pure γ-Fe$_2$O$_3$ is not useful in gas sensing applications. Instead, doped Fe$_2$O$_3$ has been used in gas sensors. For example, Tao et al.[2] reported that gas sensitivity of γ-Fe$_2$O$_3$ to alcohol was greatly improved by doping Y$_2$O$_3$ through sol-gel process. Jing [1] found enhanced sensitivity and selectivity of γ-Fe$_2$O$_3$ towards acetone, ethanol, methane, and hydrogen by doping it with zinc. Sensors utilizing γ-Fe$_2$O$_3$ have many advantages such as high sensitivity, small size, low cost, and ease of fabrication [3-6]. However, the performance stability of γ-Fe$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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$, is known to cover the surface of semiconductive metal oxides in air and eventually the variation in surface coverage of O$ 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$_2$O$_3$ nanoparticles, the free charge carriers (electrons for γ-Fe$_2$O$_3$) 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$_2$O$_3$ 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$_2$O$_3$ surface. This causes the free charge carriers captured in O$_2$ gas to move into γ-Fe$_2$O$_3$ 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$_2$O$_3$ 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(NO₃)₂·6H₂O (Zinc(III) nitrate hexahydrate, 99.9%, Alfa Aesar) and Fe(NO₃)₃·9H₂O (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-Fe₂O₃ particles were dispersed in deionized (DI) water under ultrasound sonication. The DI water suspension of the Zn-doped γ-Fe₂O₃ 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-Fe₂O₃ particles was formed over the interdigitated electrodes. A gas sensor was thus constructed. For gas sensing testing, the sensor was placed 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 2](image)

Figure 2 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.

\[
S_{signal} = \frac{R_b}{R_t} \quad (1)
\]

\[
R_{Material} = \frac{V_{Electrode}}{I_{Picoammeter}} = \frac{5.02V}{I_{Picoammeter}} \quad (2)
\]

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.

### 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](image)

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, Rₜ, to the sensing material’s electrical resistance in the present of target gas, Rₐ.

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### 4. RESULTS AND DISCUSSION

Figure 4 shows representative TEM images of Zn-doped γ-Fe₂O₃. Particle sizes of Zn-doped Fe₂O₃ formed in H₂/O₂ diffusion flame are much smaller than ones formed in H₂/Air diffusion flame.
Figure 4 represents TEM images of Zn-doped $\gamma$-Fe$_2$O$_3$ (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$_2$O$_3$ nanoparticles. However, the microparticles lost their gas sensing ability after aging.
5. CONCLUSION

Fe₂O₃ nanoparticles are formed in H₂/O₂ flames, while microparticle are formed in H₂/air flames. Gas sensors made from nanoparticles appear to be more resistant toward aging than those made from microparticles.

References