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Synthesis and characterization of Pd-doped α-Fe_2O_3 H_2S sensor with low power consumption

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Abstract

Pd-doped α-Fe_2O_3 nanoparticles were synthesized by chemical coprecipitation method and characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The gas sensing properties of undoped and Pd-doped α-Fe_2O_3 sensors were investigated. Compared with the undoped one, the doped sensors exhibited higher response, better selectivity, and faster response/recovery to H_2S. The operating temperature of α-Fe_2O_3 to H_2S is decreased after the addition of Pd, which result in the relative low power consumption in H_2S detection. Among all the doped sensors, the sensor of 1.5 wt% Pd/α-Fe_2O_3 showed the largest response (128.3) to 100 ppm H_2S at 160 °C.

Keywords: Gas sensor; Pd-doped α-Fe_2O_3; H_2S; Low power consumption

1. Introduction

The increasing concern on environmental protection and human health has generated great interests in efficient gas detection [1–3]. α-Fe_2O_3 is an n-type metal oxide semiconductor, and has been used as gas sensing material since the 1980s of the last century [4,5]. There have been many reports about good response and selectivity of α-Fe_2O_3 sensors to combustible gases and organic vapors in recent years, such as ethanol, acetone, gasoline and LPG, etc. [6,7], while their gas sensing properties to H_2S have been seldom reported until now. Recently, Zhang et al. found that α-Fe_2O_3 exhibited sensitivity to H_2S based on the catalytic chemiluminescence at 360 °C [8]. Wang et al. reported the α-Fe_2O_3 sensors synthesized by microwave hydrolysis had a high sensitivity at 300 °C [9]. However, their application is limited by the high operating temperature. As a consequence, it is important to design new type of low power consumption H_2S sensor.

Noble metal doping is an effective approach to improve the gas sensing properties of sensors. For instance, Kobayashi et al. developed CO sensor based on Au-doped α-Fe_2O_3 [10]. Shen et al. found that the response of α-Fe_2O_3 sensor to CO was greatly improved after it was doped with PdO [11]. In this paper, Pd-doped α-Fe_2O_3 nanoparticles were prepared by coprecipitation method. The gas sensing properties of the sensors were also investigated.

2. Experimental

All the reagents are of analytical grade and used as purchased.

Pd/α-Fe_2O_3 powders were prepared by a coprecipitation method [12]. A small quantity of polyglycol was added to an aqueous solution of $PdCl_2$ (0.25, 0.5, 1.0, 1.5, 2.0 and 3.0 wt%) and $Fe(NO_3)_3{\cdot}9H_2O$. The aqueous mixture was then added dropwise to an aqueous solution of Na_2CO_3 under vigorous stirring at 80 °C. The pH of the solution was adjusted by diluted Na_2CO_3 aqueous solution in the reaction process. After stirring for 1 h, a solid precipitate was formed and kept digesting overnight at room temperature. Then the precipitate was washed with deionized water, dried at 80 °C and calcined at 400 °C for an hour, a series of 0.25, 0.5, 1.0, 1.5, 2.0 and 3.0 wt% Pd-doped α-Fe_2O_3 powders were obtained.

X-ray diffraction (XRD) analyses were performed on D/MAX-RAX diffractometer operating at 40 kV and 100 mA, using Cu Kα radiation (λ = 1.5418 Å, scanning range 2*u*: 20–758). Diffraction peaks of crystalline phases were compared with those of standard compounds reported in the JCPDS Data File. Transmission electron microscopy (TEM) was carried out on a Philips–T20ST electron microscope, operating at 200 kV.

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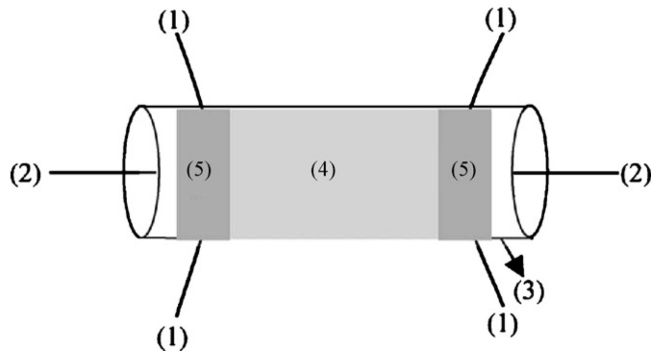

Fig. 1. Schematic diagram of the Pd/α-Fe_2O_3 thick film sensor: (1) Pt wire; (2) Ni–Cr heated wire; (3) Al_2O_3 tube; (4) Pd/α-Fe_2O_3 thick film; (5) Au electrode.

The gas sensing behavior was investigated by using the commercial gas sensing measurement system of HW-30A from Henan Hanwei Electronical Technology Co. Ltd. An alumina substrate tube with 4 mm length was used for the heater and sensing base. The schematic diagram of a typical gas sensor is shown in Fig. 1. A small Ni–Cr alloy coil was placed through the tube to supply the operating temperatures from 100 to 500 °C. Electrical contacts were made with two platinum wires attached to each gold electrode. The Pd/α-Fe_2O_3 powder was mixed with terpineol to form a paste. Then the paste was coated onto the outside surface of the alumina tube. In order to improve their stability and repeatability, the gas sensors were sintered at 300 °C for 10 days in air. Gas sensing properties of the sensors were tested in a glass chamber with a volume of 15 L. The test gases were injected into the closed chamber by a microinjector. Gas sensitivity of the side-heated gas sensors was measured under a steady-state condition. The schematic representation and the measuring principle of the gas sensor are shown in Fig. 2. The operating voltage (Vh) was supplied to either of the coils for heating the sensors and the circuit voltage (Vc = 10 V) was supplied across the sensors and the load resistor (RL = 1 MΩ) connected in series. The signal voltage across the load, which changed with sort and concentration of gas, was measured. In the gas sensitivity measurement, a given amount of sample gases were injected into a closed chamber by a microinjector and mixed by a fan for 20 s (liquids were firstly evaporated and then mixed by a fan for 20 s). The gas response S is defined as the ratio R_a/R_g, where R_a and R_g are the resistances measured in air and in a test gas, respectively.

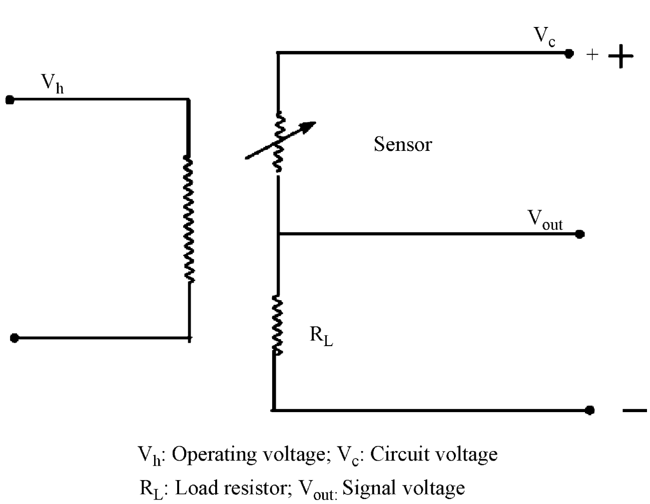

Fig. 2. Graphic of testing principle.

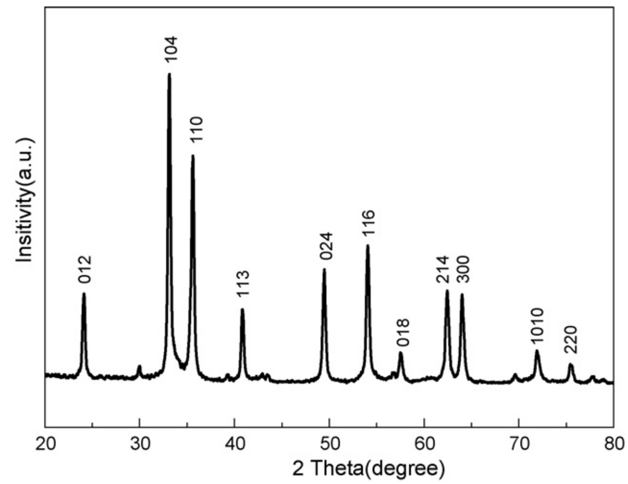

Fig. 3. XRD pattern of 1.5 wt% Pd/α-Fe_2O_3.

3. Result and discussion

3.1. Material characterization

Fig. 3 shows the XRD pattern of α-Fe_2O_3 doped with 1.5 wt% Pd additions. The diffraction pattern of α-Fe_2O_3 (1.5 wt% Pd) matched perfectly with the standard α-Fe_2O_3 reflections (JCPDS No. 33-664). However, no obvious Pd peaks was observed, which may be due to high dispersion of Pd particles. The sharp peaks suggest that the crystal of α-Fe_2O_3 is perfect. The mean size of the crystals is around 40 nm, calculated by the Deby–Scherrer equation.

TEM image of 1.5 wt% Pd/α-Fe_2O_3 is shown in Fig. 4. It can be seen that the morphology of the particles is spherical.

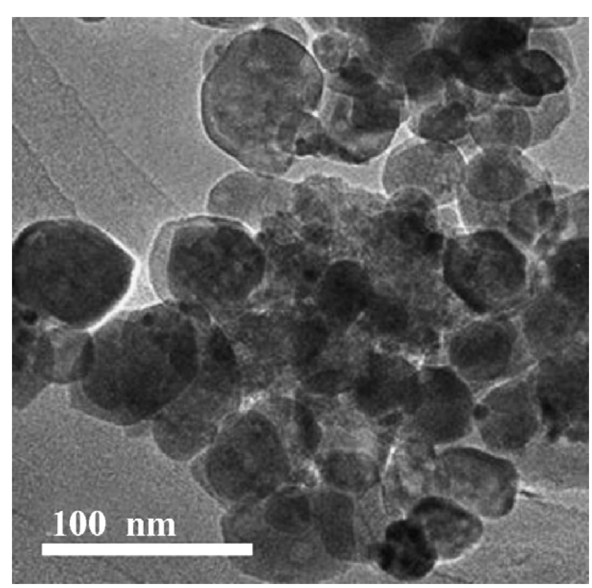

Fig. 4. TEM image of 1.5 wt% Pd/α-Fe_2O_3.