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Research paper

A novel coral-shaped Dy_2O_3 gas sensor for high sensitivity NH_3 detection at room temperature

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ABSTRACT

The coral-shaped Dy_2O_3 was prepared by a simple and environmentally friendly hydrothermal reaction combined with subsequent calcination. The coral-shaped Dy_2O_3 was assembled by clusters, which were constructed by nanoparticles, whose sizes are 12.3 ± 3.6 nm. The gas sensors were investigated with nine gases at room temperature, and show a high response and selectivity to NH_3. Compared with other reported metal oxide-based sensors, Dy_2O_3 sensor exhibits not only high sensitivity, good selectivity and reproducibility to NH_3 at room temperature, but also two good linear relationships when the concentration of NH_3 is in the range of 0.1–1 ppm and 1–100 ppm. The good gas sensing property is mainly because of the 3D hierarchical structure of coral-like Dy_2O_3, which has a large specific surface area. This benefits NH_3 molecules to adsorb/desorb onto/from the surface as well as the electron transfer. In addition, the possible NH_3-sensing mechanism is discussed in detail.

1. Introduction

Ammonia is one of the most important industrial materials. The reasonable utilization of ammonia is benefit for mankind, but the existence of ammonia is also a problem for people's lives [1,2]. Ammonia itself is a colorless gas with a strong pungent odor, which can stimulate the skin and respiratory mucosa [3]. If one breathes excessive NH_3, his lung may be swelled or even cause to death [4]. Since ammonia has a low density and volatile characteristics, if the leakage occurs, the affected area will be large [5]. Therefore, it's very necessary to monitor and control the ammonia in many environments. At present, the methods for determination of ammonia in air are general chemical analysis, spectrophotometry, gas chromatography, ammonia sensitive electrode method, direct measurement of ammonia gas analyzer and so on [6]. Most of the methods in general are not commonly used because the instruments are not convenient to carry and use except the ammonia gas detector. The detection principle of the ammonia gas detector is generally made of electrochemical or semiconductor materials, in which the metal-oxide-semiconductor has been used as the earliest ammonia sensor, due to its advantages such as a fast recovery time and response time, high repeatability, good linearity, long life, ease of manufacture and so on [7]. SnO_2 nanowires, ZnO nanorods, NiO nanowires and vanadium oxide thin film have been used as ammonia sensing materials. However, these sensors had to work at high temperature ($>300\,^{\circ}C$), which would lead to high energy consumption, poor long-term stability, narrow scope of application and so on [8–13]. In contrast, the room temperature sensor can make up for the shortcomings of high temperature sensors. Although PANI/ZnO, Co_3O_4 nanosheets and 3D hierarchical porous Co_3O_4 materials can be used as ammonia sensor at room temperature, the pure metal oxide semiconductor show low sensitivity and/or low detection limit to ammonia at room temperature now [14–16].

Dysprosium is a rare earth element, which is quite stable in the air. In the family of rare earth oxides, dysprosium oxide tends to crystallize into C-rare-earth sesquioxide structure (cubic bixbyite phase), which always exist as a structure of monoclinic and/or hexagonal [17]. Based on the characteristics arising from their 4f electrons, Dy_2O_3 nano-materials exhibit excellent physical and chemical properties. They have been widely used as the materials to control nuclear reactor, to make dysprosium lamps [18], to be anode coatings [19], and magneto-optical memory materials [20], etc. Till now, most of the investigations are concentrated on low-

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dimensional nanomaterials. The reports about 3D hierarchically structured Dy_2O_3 are relatively less. Especially the application of Dy_2O_3 in gas sensors is not found. In 2010, Pan et al. [21] reported a study of Dy_2O_3 applied on pH sensor, which evoked our concerns about Dy_2O_3 application in gas sensor.

In this paper, we synthesized pure coral-shaped Dy_2O_3 clusters by simple solvothermal route. They showed good selectivity to NH_3 and low detection limit (0.1 ppm) at room temperature. The NH_3 sensing mechanism was also discussed in detail.

2. Experiment

All the chemical reagents (analytical grade) used in the study were bought from Aladdin Reagent Net and used without further purification.

2.1. Preparation of Dy_2O_3 clusters

2.2991 g (5 mmol) of dysprosium acetylacetonate and 0.9009 g (15 mmol) carbamide were added in 25 mL methanol, in which the powders gradually dissolved with stirring. After holding the solution under stirring for 0.5 h, it was transferred into 50 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. Then cooling down to room temperature, the flavescens precursor can be gained after several rinse-centrifugation cycles with deionized water and ethanol, respectively. After the precursor was dried at 70 °C for about 10 h and followed by calcination at 500 °C in air for 2 h, white product of coral-shaped Dy_2O_3 clusters was obtained.

2.2. Characterization of coral-shaped Dy_2O_3

The phase and crystal structure of the as-prepared samples were characterized by powder X-ray diffractometer (XRD, Rigaku, D/MAX-3B) with Cu Kα1 radiation (λ = 1.54059 Å). The morphology and structure of the as-prepared samples were observed by scanning electron microscope (SEM, FEI/Philips, XL-30) and transmission electron microscope (TEM, Jeol Jem-2100), accompanied with high-resolution TEM (HRTEM) and selected-area electron diffraction (SAED) analysis. The surface areas and the Density Function Theory pore size distribution can be measured by the Brunauer-Emmett-Teller method (BET, Tristar 3020, Micrometrics Co. Ltd., USA). The sample was also analyzed by X-ray photoelectron spectroscope (XPS) (VG Scientific, ESCALAB 250) with Al Kα radiation ($h\upsilon$ = 1486.6 eV) within ± 0.2 eV deviation in the binding energy position. The C 1 s peak of the C-(C, H) component at 284.6 eV was used to calculate the binding energies according to the internal standard. The intermediate gas products produced by the exposure of the 3D Dy_2O_3 sensor to ammonia were detected by a gas chromatograph spectrometer (GC, 112A, China). The molecular sieve column used to detect N_2 is 5A (2 m × 3 mm, China) at 100 °C in H_2 flow with the velocity of 40 mL min^{-1}. H_2O can be detected by the molecular sieve column (2 m × 3 mm, TDX01, China) at 35 °C in H_2 flow with the velocity of 30 mL min^{-1}.

2.3. Fabrication of gas sensor

The Dy_2O_3 paste, pre-mixed with a small amount of terpilenol, was brush coated onto the surface of an Al_2O_3 microtube. The Al_2O_3 microtube used was 4 mm in length, 1.2 mm in external diameter and 0.8 mm in internal diameter which had a pair of Au electrodes attached with 4 Pt wires. After being dried at 70 °C for about 30 min, they were transferred into a porcelain boat to sinter at 400 °C for 1 h in air to form a thick sensing film. A heater of Ni-Cr wire was used to control the working temperature of the sensor by inserting into the Al_2O_3 microtube and housed on a six probe circular contact. The sensor was connected to the pins through soldering, and the complete sensor house with the ceramic sensor was interconnected with the sensor-test system by the six pins holder [22].

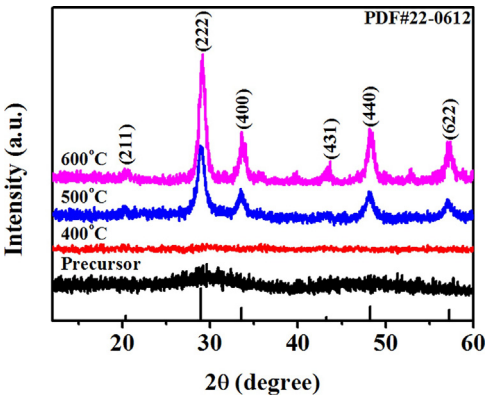

Fig. 1. XRD patterns of the as-prepared precursor and the calcined products.

2.4. Measurement of gas sensing performance

To perform measurements of gas response, a JF02E sensor test system (Kunming, China) was used by a DC method at room temperature (25 ± 1 °C). The gas sensing measurement of the sensor was carried out in a static system, the specific details of which has been given in Ref. [22]. Before measurement, a 10 L glass chamber was needed to be close to vacuum by pump in advance. Then the target gas was injected into the glass chamber with the required concentration by using different types of syringe. When we tested, air with 25 ± 1 °C and 21 ± 2% relative humidity was used as the balanced gas to make the pressure in the glass chamber the same with the outer of container. When the sensor was interconnected with the sensor-test system, a few minutes was needed to make the resistance of the sensor to reach a constant value in air. After the sensor was immediately switched into the chamber, the resistance of the sensor would decrease down to a steady value in a few minutes in the chamber. After the sensor was taken out of the chamber again, the resistance of the sensor would reach to the constant value in air. The response (S) of the sensor to target gases is defined as $S = R_a/R_g$, where R_a and R_g are the sensor resistances tested in air and in target gas, respectively. The selectivity coefficients (K_{AB}) of A gas to B gas is defined as S_A/S_B, in which S_A and S_B correspond to the response of A gas (NH_3) and B gas (triethylamine ($(C_2H_5)_3N$), paraxylene (C_8H_{10}), acetic acid ($C_2H_4O_2$), methanol (CH_4O), isopropanol (C_3H_8O), ursol (C_6H_8N), methylbenzene (C_7H_8), ammonia (NH_3) and carbon monoxide (CO)), respectively. The response time in the case of adsorption, is defined as the time required for a sensor to reach 90% of the resistance decrease ($R_a - R_g$), and the recovery time in the case of desorption, is defined as the time required for a sensor to reach 90% of the resistance increase ($R_a - R_g$). Before sensing measurement, as-prepared sensors were aged on aging equipment at 25 °C for 3 days to improve the stability of the devices.

3. Results and discussion

3.1. Structure and morphology of products

According to the TG curve (Fig. S1 a), the samples were calcined at 400 °C, 500 °C and 600 °C for 2 h. The structures of the precursor prepared by solvothermal process and the calcined product were characterized by XRD as shown in Fig. 1. It can be seen from the pattern, the intensities of diffraction peaks of the precursor are low which indicates poor crystallinity of the Dy_2O_3 precursor. In order to obtain stable Dy_2O_3 phase which show good gas sensing properties (Fig. S1b and c), the precursor was calcined at 500 °C in air for

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