Single-step controllable preparation and gas sensing performance application of claw-like indium oxide

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Abstract
In recent years, researchers attach great importance to the detection methods and materials of polluting gases, and there have been many detection of sensitive materials of different MOS (Metal oxide Semiconductor). In our work, the claw-like indium oxide material was synthesized by a single-step controllable environment-friendly method. The samples were characterized by TG, XRD, FESEM and TEM. These experimental results indicate that the synthesized sample consists of irregular nanorods with uneven surface, which were similar to claws. In addition, gas properties of claw-like In2O3 were studied, and the detection limit was up to 20 ppb, which was more significant response to nitrogen dioxide than other gases.

1. Introduction
Nanomaterials have attracted widespread attention due to their unique properties (such as physics/chemistry) and potential application prospects. It was great significance to study its microstructure and properties, to explore its formation mechanism, and to develop its application. With the global industrialization process accelerated and the rapid growth of car ownership, more poisonous, flammable, explosive and harmful gases are emitted into the atmosphere. The major pollutant NO2 emissions also continued to increase. The harm of NO2 is very serious, it can cause many problems such as photochemical smog and acid rain, also can cause cancer and respiratory disease [1, 2], which seriously endanger people’s life and property safety. In recent years, haze weather has become increasingly severe, which has affected People’s Daily life, and it has been found that the increase of NO2 emissions is an important factor for haze formation [3, 4]. Therefore, how to detect trace NO2 in the atmosphere quickly and accurately has become a worldwide concern. Atmospheric pollutant NO2 real-time monitoring could be used to understand the development trend of spatial and temporal changes of pollutant gases. It has important theoretical significance and practical value for implementing environmental management and pollution control.

There are many different methods and approaches for gas detection, such as catalytic combustion, infrared absorption spectroscopy, photoionization, ultrasonic, and solid electrolytes gas detectors. These gas detectors have long service life, wide detection range and high resolution. However, it is necessary to use neutral or very large instrument which were relatively expensive and have high environmental requirements. Therefore, we need to study gas sensor detectors with real-time monitoring, light and portable, simple and flexible. MOS gas sensor become our focus goal due to its small structure, quick response, high sensitivity and easy integration [5]. There are many materials used in semiconductor gas sensors based on MOS [6–23], such as SnO2, ZnO, Fe2O3, WO3, In2O3, NiO, CuO, TiO2/N2O5.

The shape of crystal phase, particle size and morphologies of the sensitive material have important influence on the sensing performance. Therefore, the design of In2O3 nanomaterials with different morphologies are very important. In order to meet the requirements of practical application, all kinds of In2O3 nanostructures have been synthesised, such as nanoparticles, nanowires and nanorods, nanoplates or nanosheets, and three-
dimensional architectures. However, Gas-sensing property not only dependent on the diverse composition of material elemental, but also on properties of material surface, the interactions between the atoms, the size of the constituent ions. Now, more researcher pay attention to one-dimensional materials because its unique special characteristics of nanoparticles, photoconductive property, thermal stability, field emission effect, admirable electron transfer, etc. One-dimensional materials including nanorods, nanocable, nanodendrite, nanobelts, nanotubes and nanofibers.

With the development of technology and people’s pursuit of high quality life, we hope that we can prepare nano-gas sensitive materials which we need through low-cost and low-pollution methods. Indium oxide (In$_2$O$_3$) as typical and important n-type wide band-gap MOS, has been investigated for its gas sensitivity properties of VOCs, H$_2$, O$_3$, Cl$_2$, H$_2$, S, SO$_2$, NH$_3$ and NO$_2$. In this work, we produced claw-like In$_2$O$_3$ by a low-cost environmentally friendly method. The as-obtained claw-like In$_2$O$_3$ exhibited excellent gas sensitive property for NO$_2$, which have potential application value for NO$_2$ detect in the atmospheric environment.

2. Experimental

2.1. Materials
Indium nitrate In(NO$_3$)$_3$·4.5H$_2$O (AR, ≥99.5%), ethanol C$_2$H$_5$OH (AR, ≥99.7%), Sucrose (AR), Urea (AR, ≥99.0%). All the reagents used as received without any further purification.

2.2. Preparation of precursor
First, prepare the mixed solution ethanol/water = 1:1. Second, In(NO$_3$)$_3$·4.5H$_2$O, 2.92 mmol sucrose and 2.49 mmol urea were added into the solution, then stirring and ultrasonic alternating treatment two hours. Third, transferred the uniformly mixed solution to teflon-lined stainless steel autoclave, then kept constant temperature for twelve hours.

2.3. Precursor collection
After the stainless steel autoclave was naturally cooled, we separate used the centrifuge and washed the precipitates repeatedly, then dried at 80 °C for twelve hours. After this treatment we get the black precursor.

2.4. Sample calcined
The precursor were calcined for two hours in muffle furnace and faint yellow samples were collected.

2.5. Gas sensors manufacture
The faint yellow sample powders were mixed with absolute ethanol to form a thin film on the ceramic tube. The gas sensor devices were calcined and then aged to eliminate the effect of impurities on gas sensitivity. The graph of gas sensor device was shown in figure 1.

3. Results and discussion

3.1. Structural composition of the obtained faint yellow samples
Thermogravimetric (TG) curves are shown in figure 2(a). From TG curve, we know that first weight loss 5.2% between 30 °C–140 °C, corresponded to physical water evaporation and organics such as ethanol weak adsorption to the surface of as-prepared precursor. Secondly, between 140 °C–600 °C, was ascribed to the decomposition of carbon content and the crystal chemical dehydration of precursor sample. Therefore, In$_2$O$_3$ products can be obtained by calcination of the as-prepared black precursors. Figure 2(b) shows the x-ray powder diffraction patterns of our faint yellow sample powders. All the prominent peaks in the patterns correspond to cubic structure In$_2$O$_3$ [19, 20] and are indexed on the basis of JCPDS (No. 89-4595). No peak corresponding to the doping material was found.

Figure 3 field emission scanning electron microscopy (FESEM) images of the claw-like In$_2$O$_3$ with different magnification. Figure 3(a) low magnification reveals that those nanorods cluster have a rough surface with length of 100 nm. The figure shown that no other topographical structures were found. Figures 3(b)–(d) shows the morphology at an enlarger-magnification FESEM, these nanorods cluster form a shape similar to the dragon’s claw, and the clutches are made of particles. Transmission electron microscopy (TEM) images of as-synthesized In$_2$O$_3$ nanorods cluster, were consistent with SEM. Results shown that the diameter of the were about 100 nm in figures 4(a), (b). HRTEM image as shown as in figure 4(c), fringe distance of the In$_2$O$_3$ nanorod cluster was 0.292 nm, corresponding with the lattice distances (222) plane of hexagonal indium oxide (PDF No.
3.2. Gas sensitivity properties of the materials for NO$_2$

The gas sensitivity properties were determined under this condition ($50\% \pm 10\%$ RH, $23 \pm 1 \degree C$) [12, 19]. The Response $R_{\text{gas}}/R_{\text{air}}$ for oxidizing gas and $R_{\text{air}}/R_{\text{gas}}$ for reducing gas, $R_a$ and $R_g$, were the resistances in the air and different gases which will be measured. The sensor response times and recovery times during the gas sensing test was calculated based on 90% of the total resistance which changed during the adsorption and desorption processes, respectively.
For comparison, we performed gas sensitivity tests on In$_2$O$_3$ sensitive materials obtained (figure 5) with urea and without urea (abbreviated as S1 and S2) were investigated. It can be seen from figure 5(a), under the condition that only sucrose was added without urea, we obtained non-uniform hollow spherical structure In$_2$O$_3$. Under the condition that both sucrose and urea were added, we obtain claw-like In$_2$O$_3$ composed of small-sized surface-roughened nanorod clusters. It is also proved that the presence of sucrose and urea has a great influence on the formation of the final morphology. In the formation of claw-like In$_2$O$_3$, urea may play
ternary roles, including being the alkaline media, the coordinating agent and the surface anchored organic molecules [21].

According to previous reports and experimental evidence, gas response of MOS is highly influenced by actual operating temperature [5, 12, 22, 23]. In order to determine an optimum operating temperature, the response of the sensors towards 500 ppb NO2 was examined as a function of operating temperature. The correlation of the response and response time of the sensor based on S1 and S2 to 1 ppm NO2 with the operating temperature was measured over the range 50 °C–250 °C and shown in figure 6(a). The response decreases in the initial stage at very low temperatures then increases in the intermediate stage and the response decreases when the actual operating temperature transcend 125 °C (sensor S1) and 150 °C (sensor S2). It should be noted that

Figure 5. FESEM images of In2O3 products synthesized with the presence of different amounts of urea of (a) 0 g, and (b) 2.49 mmol, respectively.

Figure 6. (a) Response of the sensors to 1 ppm of NO2 as a function of operating temperature. (b) Repeated response curves and (c) Response transients curve and to 1 ppm NO2 for the sensor as-synthesized claw-like In2O3 at the operating temperature of 150 °C. (d) Responses to different concentrations of NO2 for the sensor using the claw-like In2O3 at 150 °C.
although gas response was relatively high at low temperatures (such as below 50 °C), but the response time is too long. The optimum operating temperature of S1 was 125 °C, S2 was 150 °C, respectively. The working temperature of the sensor, regulating the adsorption/desorption processes at equilibrium and the competition for chemisorption between NO2 and atmospheric oxygen O2 for the same active surface sites, play an important role in determining the specific interaction between NO2 and the sensing material. In the following research application, the temperatures of S1 and S2 were also based on the optimum operating temperature.

The response recovery time and repeatability were also extremely important criterions for judging the performance of gas sensor device. The five reversible cycles of the response curve indicated a stable and repeatable response characteristic, as shown in the inset of figure 6(b). It can be observed that the average response obtained was 88 to 1 ppm NO2. The response transients of the claw-like In2O3 (S2) sensor to 1 ppm NO2 was measured at 150 °C (figure 6(c)). Response and recovery times were approximately 30 s and 18 s. Figure 6(d) shown the gas responses to different concentrations of NO2 for the sensor using the claw-like In2O3 (S2) at 150 °C. The resistance increase when exposure to NO2 atmosphere and compliance with the gas-sensitive response behavior of n-type MOS.

The relationship between gas response and NO2 concentration range 20 ppb–2 ppm was shown in figure 7(a). It could be clearly seen that as the concentration of the oxidizing gas NO2 increases, the gas response value increases, and S2 exhibited superior characteristic than S1. The sensor S2 detection limit was as low as 20 ppb, and the value of gas response was 2.1. The response was about 5.6, 10.6, 19.8, 32.8, 45.8, 88 and 145 to 50, 100, 200, 300, 500, 1000 and 2000 ppb NO2, respectively. Figure 7(b) shown the gas response of claw-like In2O3 to various target test gases. It could be seen clearly that S2 based on claw-like In2O3 has the highest response to NO2 and the response to other gases were relatively weak. It should be noted that if gas sensors want to be applied in practice, long-term stability must be considered, so we tested the stability and reliability of our device. Under the same conditions, we tested the resistance in the air and gas-sensitive property in NO2 atmosphere in 40 experimental test days. The air resistance and their corresponding gas responses did not significantly float within
40 test days at optimum temperature 150 °C in figures 7(c) and (d), meant that the claw-like In$_2$O$_3$ gas sensor has excellent long-term stability and reliability.

From the above test results, the claw-like In$_2$O$_3$ sensor can be practically applied. The response process of claw-like In$_2$O$_3$ as typical n-type MOS can be interpreted [24–29]: when the sensor was exposed to NO$_2$ atmosphere, large amounts of oxygen will absorb onto the surface of the MOS. The adsorbed oxygen molecules capture electrons from the material's conduction band (NO$_2$ (gas) + e$^-$ → NO$_2$ (ads) and ) and convert them into more active chemically adsorbed oxygen species (NO$_2$ (gas) + 2O$_2$ (ads) → NO$_2$ (ads) + O$_2$ (gas) + e$^-$ and NO$_2$ (gas) + O$_2$ (ads) → NO$_2$ (ads) + 2O$_2$ (ads)), creating a space charge zone (depletion layer) in the material that increases sensor’s resistance in NO$_2$ atmosphere. The Claw-like In$_2$O$_3$ composed of coarse nanorods cluster with uniform size and abundant surface active sites. This structure allows the tested gas to diffuse well, thereby performing physical and chemical adsorption [30–33].

4. Conclusion

In short, claw-like In$_2$O$_3$ with faint yellow were prepared by solvothermal method and suitable calcining process. SEM and TEM results that the claw-like In$_2$O$_3$ were composed of coarse nanorods cluster with uniform size and abundant surface active site. The gas-sensitive properties of claw-like In$_2$O$_3$ were researched. The sensor exhibits excellent long-term stability and reliability. The sensor detection limit was as low as 20 ppb, and the value of gas response was 2.1 at optimum temperature 150 °C. From the above test results, the sensor based on claw-like In$_2$O$_3$ might have potential application because it has the advantages of high sensitivity, low response time, low power consumption.

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