1D N-type SnO$_2$ nanofibers coexisted with P-type Co$_3$O$_4$ cubes for highly selective acetone sensor

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Abstract. 1D n-type SnO$_2$ nanofibers coexisted with p-type Co$_3$O$_4$ particles were synthesized by electrospinning with subsequent hydro-thermal process. The morphology and composition of Co$_3$O$_4$/SnO$_2$ were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM). XRD patterns showed that the synthesized Co$_3$O$_4$/SnO$_2$ were assigned to cubic Co$_3$O$_4$ and tetragonal rutile structure of SnO$_2$ without any other impurity peaks. A possible growth mechanism was proposed to describe the formation of hierarchical SnO$_2$ nanofibers coexisted with Co$_3$O$_4$ cubes. The Co$_3$O$_4$/SnO$_2$ compound exhibited a relatively highly selective response to acetone and stable acetone sensing performance after a long period of aging. The Co$_3$O$_4$/SnO$_2$ compound had a p-type response. It may be ascribed to the high coverage of p-type Co$_3$O$_4$ on n-type SnO$_2$. The excellent acetone sensing properties of Co$_3$O$_4$/SnO$_2$ nanostructures may be attributed to p-n junctions between Co$_3$O$_4$ and SnO$_2$ nanograins as well as the unique coexistence structure of nanofibers and cubes.

1. Introduction

Acetone as a widely used industrial raw material is regarded as a huge threat to human’s health especially exposure to high concentration over 100000 ppm. It is reported that the acetone concentration in exhaled breath of diabetic patients is much higher than healthy people [1]. Therefore, in consideration of health and safety, there is a huge demand for detecting acetone concentration in public or human body.

Currently, a lot of metal oxide semiconductors (MOS) have been applied to detect harmful and toxic gases. These sensors based on MOS have many advantages such as high sensitivity, short respond/recovery time and simple synthesis route, but they also have disadvantages of poor selectivity, high operating temperature and low sensitivity to ultra-low concentrations of gases [2]. Several strategies including the use of compound metal oxides [3, 4], heterostructure formation [5, 6], transition metal catalyst doping [7, 8] and UV light irradiation [9] have been used to overcome these drawbacks. For example, surface modification with noble metal (Au, Pd, Ag) nanoparticles as sensitizer is the most common approach to improve the gas sensing properties due to the catalytic overflow effect of noble metal particles. Meanwhile, the p-n heterojunction method is also an effective strategy to improve gas sensitive parameters of SnO$_2$-based gas sensors. P-n heterostructures can be obtained by mixing compound structures, forming core-shell structures, decorating with second-phase particles and building bi-layer or multi-layer films [10].
P-type Co$_3$O$_4$ with a direct band gap of about 2 eV, is one of most interesting materials with huge potential applications such as lithium-ion batteries [11], VOC gas sensors [12], catalyst [13], electrochemistry [14], supercapacitor [15]. So far various methods have been developed to synthesize Co$_3$O$_4$ with different nanostructures such as nanocubes [16], nanosheets [17, 18], and nanofibers [19]. It is considered as an excellent active material loaded on a host oxide due to its good conductivity, high catalytic reactivity, stable chemical activity [20], and its special structure which facilitates electron transportation between Co$^{2+}$ and Co$^{3+}$ ions. However, in the field of gas sensors, a serious shortcoming of low sensitivity has limited the application of Co$_3$O$_4$ in actual implementation. Up to now, numerous modification methods have been adopted to improve the gas sensing characteristics of Co$_3$O$_4$ as a high sensitive material at low operating temperature. Among them, compositing with n-type semiconductor is a good choice because it not only strengthens the interactions of closely packed nano-units but also extends the electron depletion layer by forming p-n heterojunctions [21, 22]. As is known to all, SnO$_2$ is a typical n-type semiconductor with excellent gas sensing properties except the poor selectivity.

In this study, n-SnO$_2$ NFs coexisted with p-type Co$_3$O$_4$ cubic nanoparticles were synthesized by electrospinning with subsequent hydrothermal process. The acetone gas sensing properties were tested. In particular, the origin of the enhanced acetone response of Co$_3$O$_4$/SnO$_2$ compared to pure Co$_3$O$_4$ is discussed from the perspective of p-n heterojunctions [23].

2. Experimental details

2.1. Synthesis of material

**Synthesis of SnO$_2$ nanofibers.** SnO$_2$ NFs were synthesized by simple electrospinning that our group reported before [24]. Briefly, 1 mmol of SnCl$_2$·2H$_2$O were dissolved in 4.2 mL of EtOH solvent at room temperature with magnetic stirring for 30 minutes. Subsequently, a certain amount of PVP and 3.5 mL of DMF were added into above solution, agitating for 8 h. The relevant parameters were as follows: the voltage and the distance between the needle (positive pole) and the collector (negative pole) were 18 kV and 15 cm, respectively. The diameter of the needle was 0.7 mm.

**Synthesis of Co$_3$O$_4$ cubic nanoparticles.** Co(NO$_3$)$_3$·6H$_2$O, CTAB, methanol were of analytical grade, without further purification. 4 g Co(NO$_3$)$_3$·6H$_2$O and 2 g CTAB were dissolved in 12 mL deionized water and 60 mL methanol, sonication for 30 min. The solution was transferred to 100 mL Teflon autoclaves and heated at 180 for 24 h. The products were obtained by centrifugation and annealed at 600°C for 3 h.

**Synthesis of Co$_3$O$_4$/SnO$_2$ heterostructures.** 0.05 g SnO$_2$ NFs with annealed at 600°C for 3 h were added into the Co$_3$O$_4$ hydrothermal solution. Hydrothermal reaction process is the same as the second step.

2.2. Fabrication and measurement of gas sensors

The fabrication and gas sensing test of the sensors were the same as our group reported before [22], as shown in Figure 1. The sintered samples were mixed with a suitable amount of deionized water and then grinded for 30 min to form a paste. The paste was coated on a clean ceramic tube with a pair of gold test electrodes. After that the ceramic tubes were sintered at 500°C for 3 h in air. Subsequently, a Ni-Cr heating wire was inserted into the tube to fabricate a side-heating gas sensor. Before testing gas sensing properties, the fabricated sensors should be aged at 300°C for 7 days in air to improve device stability. The gas sensing properties were measured in a range of 100°C~200°C in a home-built static test system. The response of n-type sensor was defined as S=Ra/Rg while p-type sensor is the opposite, of which Ra and Rg referring to the stable resistance values in air and in target gas, respectively.

2.3. Characterizations

The Co$_3$O$_4$/SnO$_2$ heterostructures were analyzed by XRD (Shimadzu XRD-6000, Japan) in 2θ region of 20-80° with Cu Kα 1 (0.15406 nm) radiation. Scanning electron microscopy (SEM) was carried out...
on a FEI QUANTA 200F (USA) microscope equipped with energy-dispersive X-ray (EDX) spectroscopy.

![Diagram of synthesis process]

Figure 1. Schematic of synthesis, fabrication and sensing test of Co$_3$O$_4$/SnO$_2$ based sensors.

3. Results and discussion

3.1. X-ray diffraction (XRD)

Figure 2 presents the XRD patterns of Co$_3$O$_4$ and Co$_3$O$_4$/SnO$_2$. All the peaks of Co$_3$O$_4$ were assigned to cubic cobalt oxide with lattice constants of a=b=c=8.118 Å (PDF#80-1534). All the diffraction peaks of pure SnO$_2$ can be indexed to pure tetragonal rutile structure of SnO$_2$ (PDF#77-0452). In the XRD pattern of Co$_3$O$_4$/SnO$_2$, in addition to the reflections from Co$_3$O$_4$, peaks from (110), (101), (211), (220) and (321) lattice planes of SnO$_2$ with lattice constants of a= 4.755 Å were identified. No diffraction peaks from any other impurities were observed. The continuous diffraction peaks indicates that the synthesized samples become essentially amorphous after high temperature calcination.

![XRD patterns of Co$_3$O$_4$ and Co$_3$O$_4$/SnO$_2$]

Figure 2. XRD patterns of Co$_3$O$_4$ and Co$_3$O$_4$/SnO$_2$. 
3.2. Scanning electron microscopy (SEM)
The morphology of Co$_3$O$_4$, Co$_3$O$_4$/SnO$_2$ and SnO$_2$ were investigated by SEM characterization. From Figure 3(a) and (b) it can be seen that Co$_3$O$_4$ have a clearly cube structure. The observed six planes of nanocubes are bound by planes of Co$_3$O$_4$ crystal with spinel structure [16]. However, when loading Co$_3$O$_4$ cubic nanoparticles with SnO$_2$ nanofibers, cubic Co$_3$O$_4$ decomposed into blocks. Meanwhile Co$_3$O$_4$/SnO$_2$ exhibited a special morphology of coexistence of blocks and fibers, of which fibers are SnO$_2$ and blocks are Co$_3$O$_4$, as shown in Figure 3(c). Figure 3(d) shows that the SnO$_2$ nanofibers prepared by electrospinning is one dimensional and has hollow hierarchical structure. It further indicates that the introduction of different metal oxide with opposite conductive type has a great influence on the morphology of the main materials.

![Figure 3. SEM images of (a) Co$_3$O$_4$ cubes, (b) individual Co$_3$O$_4$ cube, (c) Co$_3$O$_4$/SnO$_2$ compound and (d) SnO$_2$.](image)

3.3. Growth process and acetone sensing properties
Figure 4 is the schematic illustration for possible formation processes of SnO$_2$ nanofibers, cubic Co$_3$O$_4$ and Co$_3$O$_4$/SnO$_2$. For SnO$_2$ nanofibers, Sn$^{2+}$, Cl$^-$, NO$_3^-$ and PVP chain are evenly mixed to form compound nanofibers in the electrospinning period. When heating treatment, the anions are decomposed by oxidation while the cations are oxidized and crystallized into small particles, agglomerate into big ones and connect together to form nanofibers eventually. With post-heat treatment, the unstable Co$_3$O$_4$ precursor recrystallized into Co$_3$O$_4$ with a stable cube structure. For Co$_3$O$_4$/SnO$_2$ structures, the as synthesized SnO$_2$ nanofibers were added into the Co$_3$O$_4$ hydrothermal solution to mix uniformly. During the hydrothermal reaction process with high temperature and high pressure, the Co$_3$O$_4$precursor and SnO$_2$ recrystallized to form heterojunction structure.

Figure 5 indicates the responses of the Co$_3$O$_4$ and Co$_3$O$_4$/SnO$_2$ gas sensors as a function of operating temperature in a range of 100–200°C and the acetone concentration is 10 ppm. The sensitivities of Co$_3$O$_4$ and Co$_3$O$_4$/SnO$_2$ gas sensors were highest at 150°C. Therefore, 150°C was chosen as optimal operating temperatures for both Co$_3$O$_4$ and Co$_3$O$_4$/SnO$_2$ gas sensors in the following gas sensing measurement. The maximum responses of the sensors at 150°C may be ascribed to the different activation energies of pre-adsorbed surface oxygen species at different temperatures.

Figure 6(a) and (b) show the sensitivities of gas sensors based on Co$_3$O$_4$ and Co$_3$O$_4$/SnO$_2$ to different acetone concentrations in a range of 1–75 ppm at operating temperature of 150°C, respectively. It can be seen that the response of the gas sensor based on Co$_3$O$_4$/SnO$_2$ compound is much higher than that of gas sensor based on Co$_3$O$_4$ cubic nanoparticles. Once upon exposure to acetone, the resistances of the two sensors increase rapidly, exhibiting typical p-type conductivity. However, the resistances of both sensors could return to initial resistance level upon removing acetone.
Meanwhile, for different cycles of injecting-releasing acetone, both sensors can recover to their initial states, indicating a good reproducibility of Co$_3$O$_4$ and Co$_3$O$_4$/SnO$_2$ sensors. With the increasing of acetone concentration, the sensor based on Co$_3$O$_4$/SnO$_2$ presents good response to acetone, showing a relatively good linear response-concentration relationship while the response values of Co$_3$O$_4$ increase exponentially with acetone concentration, showing nonlinear response characteristics. Figure 7 is the response/recovery curve of Co$_3$O$_4$/SnO$_2$ based sensors to 20 ppm acetone. According to the definition of response time and recovery time, the response/recovery time of Co$_3$O$_4$/SnO$_2$ based sensors are 44 s and 23 s respectively.

**Figure 4.** Schematic illustration for possible formation processes of SnO$_2$ nanofibers, cubic Co$_3$O$_4$ and Co$_3$O$_4$/SnO$_2$.

![Figure 4](image_url)

**Figure 5.** Responses of Co$_3$O$_4$ and Co$_3$O$_4$/SnO$_2$ gas sensors vs operating temperatures.

![Figure 5](image_url)
Selectivity is an important gas sensing parameter for practical gas sensors. The improvement of selectivity mainly depends on the development of new sensitive materials and the use of catalysts. In this work, the sensitivity of Co$_3$O$_4$ based sensors is improved by the introducing of SnO$_2$. The responses of Co$_3$O$_4$ and Co$_3$O$_4$/SnO$_2$ gas sensors to five interference gases including formaldehyde, ethanol, toluene, methanol and ammonia with a concentration range of 10 ppm were examined, as shown in Figure 8. The response of the Co$_3$O$_4$/SnO$_2$ gas sensor to acetone is higher than the sensitivities to the other interference gases. Therefore, it can be concluded that the Co$_3$O$_4$/SnO$_2$ gas sensor has a good selectivity to acetone. Meanwhile, the selectivity of Co$_3$O$_4$/SnO$_2$ is better than that of Co$_3$O$_4$. 

Figure 6. Dynamic response curves of (a) Co$_3$O$_4$ cubes, (b) Co$_3$O$_4$/SnO$_2$ to acetone in a range of 1-75 ppm.

Figure 7. Response/recovery curves of Co$_3$O$_4$/SnO$_2$ based sensors to 20 ppm acetone.
Figure 8. Responses of Co₃O₄ and Co₃O₄/SnO₂ gas sensors to different gases.

Figure 9 gives the long-term stabilities of Co₃O₄ and Co₃O₄/SnO₂ gas sensors in 10 ppm acetone vapor with a measurement temperature range of 10~15°C. From the curves we can see that the response of Co₃O₄/SnO₂ based sensors has picked up after four weeks’ aging while the response of Co₃O₄ continues to decrease. On the whole, the responses of Co₃O₄/SnO₂ based sensors do not change very much in this time range, indicating a good stability of the fabricated sensors.

Figure 9. Long-term stabilities of Co₃O₄ and Co₃O₄/SnO₂ based sensors to 10 ppm acetone over 4 weeks.

In addition, the sensing properties of our fabricated Co₃O₄/SnO₂ gas sensors are compared with other published Co₃O₄/SnO₂ gas sensors, as shown in Table 1. It can be seen that the sensing properties of our fabricated Co₃O₄/SnO₂ gas sensors are comparable to those of the previously reported Co₃O₄/SnO₂ sensors. For example, the optimal working temperature of our fabricated Co₃O₄/SnO₂ gas sensors is lower than Co₃O₄-decorated SnO₂ nanowires [25], Co₃O₄/SnO₂ compound [26] and Co₃O₄-loaded SnO₂ thick films [27]. According to different microstructures, components and synthesis methods, the gas sensing response of Co₃O₄/SnO₂ based sensors can be either p-type or n-type. However, most of the test gas species of the reported Co₃O₄/SnO₂ based sensors are oxidized gases.
and hydrogen, few VOC gases were measured. The higher response of [28] and [29] may be attributed to the difference relative molecular mass of gases. It has been reported that smaller molecules can interact and diffuse more efficiently on the surface of sensitive materials than others with greater molecular mass [30]. Even though certain sensing parameters of our fabricated Co$_3$O$_4$/SnO$_2$ based sensors are not as good as the previously reported, the gas sensing abilities of the synthesized Co$_3$O$_4$/SnO$_2$ can be improved by optimizing grain size through modulating the temperature and time of hydrothermal reaction and calcination in the future work.

3.4. Sensing Mechanism

As known to all, the pre adsorbed oxygens in air play an important role in the gas sensing reaction. In an air environment at the optimum operating temperature, the oxygen molecules will be adsorbed on the surface of the semiconductor metal oxides and extract electrons to form adsorbed oxygen species such as O$_2^-$, O$^-$ and O$_2^{2-}$. At the same time, a depletion layer and junctions are formed at the grain boundaries.

For Co$_3$O$_4$/SnO$_2$, lots of Co$_3$O$_4$/SnO$_2$ heterojunctions are simultaneously generated in addition to the SnO$_2$/SnO$_2$ homojunctions, as shown in Figure 10. When n-type SnO$_2$ and p-type Co$_3$O$_4$ nanograins come into contact, electrons will flow from n-type SnO$_2$ to p-type Co$_3$O$_4$ until the Fermi level on each side reached an equilibrium, forming an hole depletion layer on the Co$_3$O$_4$ side and an electron depletion layer on the SnO$_2$ side. As a result, the resistances of Co$_3$O$_4$/SnO$_2$ increased greatly. Upon exposure to acetone, as both SnO$_2$ and Co$_3$O$_4$ have reactivity to acetone, the electrons are given back to the conduction bands of SnO$_2$ and Co$_3$O$_4$. It results in the decrease of band bending in SnO$_2$. However, because Co$_3$O$_4$ is almost inactive to acetone, the conduction band of Co$_3$O$_4$ remained almost unchanged. Therefore the height of potential barriers in Co$_3$O$_4$/SnO$_2$ increased. In this way, the resistance of Co$_3$O$_4$/SnO$_2$ sensors towards acetone increased and showed a p-type response. The additional resistance change of Co$_3$O$_4$/SnO$_2$ is the main factor of enhanced gas sensing properties of Co$_3$O$_4$/SnO$_2$.

![Figure 10. The possible sensing mechanism model for Co$_3$O$_4$/SnO$_2$-based sensors.](image-url)
Table 1. Comparison of sensing properties of our Co$_3$O$_4$/SnO$_2$ sensors with previously reported Co$_3$O$_4$/SnO$_2$ sensors.

| Structures                        | Gas species | Concentration (ppm) | Operating temperature (°C) | Response & conductive type | Reference |
|-----------------------------------|-------------|---------------------|-----------------------------|----------------------------|-----------|
| Co$_3$O$_4$-decorated SnO$_2$ nanowires | NO$_2$      | 2-10                | 300                         | 3.5/10 ppm p-type          | [25]      |
| Co$_3$O$_4$/SnO$_2$ composites    | H$_2$       | 5-200               | 300                         | -- p-type                  | [26]      |
| Co$_3$O$_4$/SnO$_2$ system        | CO          | 20-1000             | 25                          | 192/1000 ppm p-type        | [28]      |
| Co$_3$O$_4$/SnO$_2$ thick films   | CO          | 10                  | 250                         | 100 n-type                 | [29]      |
| Co$_3$O$_4$-loaded SnO$_2$ thick films | alcohol  | 1000                | 300                         | 301 n-type                 | [27]      |
| SnO$_2$ nanofibers loaded with p-type Co$_3$O$_4$ cubic | acetone     | 10                  | 150                         | 3.7 p-type                 | this work |

4. Conclusions
To put it generally, n-SnO$_2$ nanofibers coexisted with p-Co$_3$O$_4$ cubes were synthesized by electrospinning with subsequent hydrothermal process, and their acetone sensing properties were tested. The Co$_3$O$_4$/SnO$_2$ exhibited a relatively highly selective response to acetone and stable sensing performance. Meanwhile, the sensing response of the Co$_3$O$_4$/SnO$_2$ manifested as Co$_3$O$_4$ do, namely p-type response. It may be ascribed to the high coverage of p-type Co$_3$O$_4$ on n-type SnO$_2$. The origin of the enhanced acetone response of Co$_3$O$_4$/SnO$_2$ is attributed to p-n heterojunctions between Co$_3$O$_4$ and SnO$_2$ nanograins as well as the unique structure of coexistence of Co$_3$O$_4$ cubics and SnO$_2$ nanofibers. This work may be helpful for clarifying the gas sensing mechanism in p-n heterojunctions.

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